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USSR Report

CHEMISTRY

No. 106



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UDC 543.45

IDENTIFICATION AND QUANTITATIVE DETERMINATION OF TRICHOTHECENE MYCOTOXINS
BY CAPILLARY GAS CHROMATOGRAPHY

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 38, No 5, May 83
(manuscript received 19 Apr 82) pp 903-907

ELLER, K. I. and SOBOLEV, V. S., Institute of Nutrition, USSR Academy of
Medical Sciences, Moscow

[Abstract] A simple method was described for synthesis of trifluoroacetyl (TFA) derivatives of trichothecenes, for which capillary gas chromatographic separation on polysiloxane liquid phase OV-101 was developed and a quantitative determination of TFA derivatives of trichothecenes was achieved, using n-tricosane as an internal standard. This method permits detection of 100-200 μ g of the mycotoxin per one kg of the grain tested. Figure 1; references: 10 Western.
[292-7813]

UDC 543.53

INSTRUMENTAL NEUTRON ACTIVATION DETERMINATION OF URANIUM USING CALIFORNIUM
AS NEUTRON SOURCE

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 38, No 5, May 83
(manuscript received 25 Jan 82) pp 862-864

IVANENKO, V. V. and METELEV, A. Yu., Institute of Chemistry, Far East
Scientific Center, USSR Academy of Sciences, Vladivostok

[Abstract] Instrumental neutron activation method for determining uranium content in sea water has the disadvantage of being dependent on physically remote neutron generating sources. A method was developed for determination of uranium extracted from sea water using ^{252}Cf radioisotope as the neutron generator, so that the analysis could be performed on board ships. The neutron yield was $4 \cdot 10^9$ n/sec; optimal test conditions provided for a 40 min exposure to neutrons and 40 min counting time. It was shown that, in order to be effective, a 3 orders-of-magnitude concentration of uranium above the water level must have been achieved, i.e., from $10^{-7}\%$ predominant in sea water to

$10^{-4}\%$ in the test sample. The sensitivity of this test is $24\text{ }\mu\text{g}$ in a 20 g absorbent, or $1.2 \cdot 10^{-4}\%$. Figures 2; references: 5 (Russian, one by Western authors).
[297-7813]

UDC 543:551.510.04

DETERMINATION OF HYDROGEN CYANIDE IN ATMOSPHERIC AIR WITH SAMPLING ON SOLID ADSORBENT

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 38, No 5, May 83
(manuscript received 16 Nov 81) pp 797-801

VOL'BERG, N. Sh., KUZ'MINA, T. A. and STOLYAROV, K. P. (deceased), Main Geophysical Observatory imeni A. I. Voyeykov and Leningrad State University imeni A. A. Zhdanov

[Abstract] The goal of this study was to find an improved air sampling method suitable for field conditions. A solid adsorbent was selected: crushed glass particles (1-2 mm in size) impregnated with 50% aqueous NaOH solution. This method permitted trapping HCN at a flow rate of $0.5-6\text{ dm}^3/\text{min}$, HCN in the test samples ranging from 1 to 5.8 mg and a collection time of 20 min to 24 hrs. Under these conditions the escape of HCN through the trap was less than 2.5%. The method yields highly reproducible results. Figures 4; references 17: 5 Russian, 12 Western.
[292-7813]

UDC 543.31:542.61:546.815:546.47

EXTRACTION-ATOMIC ABSORPTION DETERMINATION OF LEAD AND ZINC IN SEA WATER

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 38, No 5, May 83
(manuscript received 1 Jul 82) pp 835-840

OSIPOV, N. N., CHARYKOV, A. K. and PANICHEV, N. A., Leningrad State University imeni A. A. Zhdanov

[Abstract] Developmental results were reported on extraction-atomic absorption method of determining microquantities of lead and zinc in sea water which made it possible to extract quantitatively these metals in one step, yielding stable extracts and permitting direct injection of the test sample into the electrothermal atomizer. Monobasic pelargonic acid was used as the extraction solvent yielding stable extracts suitable for extended storage. The method is selective for Pb and Zn; the complexes formed are $\text{Na}_2\text{PbR}_4 \cdot 4\text{H}_2\text{R}_2$ and $\text{ZnR}_2 \cdot 2\text{H}_2\text{R}_2$ where H_2R_2 stands for oekargibuc acid. Sensitivity of this method is $0.1\text{ }\mu\text{g/lit}$. Figures 5; references: 12 (Russian, one by Western authors).
[252-7813]

GAS CHROMATOGRAPHIC DETERMINATION OF DIKURAN AND DOZANEX HERBICIDES

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 38, No 5, May 83
(manuscript received 5 Apr 82) pp 908-911

KIRICHENKO, V. Ye., PASHKEVICH, K. I. and KULIKOVA, G. S., Institute of Chemistry, Ural Scientific Center, USSR Academy of Sciences, Sverdlovsk

[Abstract] Introduction of new herbicides into agriculture: chlorotolurone (Dikuran) and methoxurone (Dozanex) necessitated development of new analytical methods for determination of their residual levels in the environment. Gas chromatographic separation of these agents was investigated using electron capture detector. It was shown that Dikuran and Dozanex could not be effectively separated on siloxane columns. These compounds had to be first converted to 3-trifluoromethoxy-2,2,3,3-tetrafluoropropionic acid anilides to permit their determination in water, soil and in plants. Detection limits were 0.002 mg/l in water and 0.02 mg/kg in soil and in plants. Figure 1; references 7: 3 Russian, 4 Western.
[292-7813]

UDC: 547.341

CONFORMATION STRUCTURE OF 1,3-ALKADIENEPHOSPHONATES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 5, May 83
(manuscript received 17 Dec 82) pp 1186-1187

RATOVSKIY, G. V., SERGIYENKO, L. M., BREL', V. K., MASHLYAKOVSKIY, L. N., and IONIN, B. I., Leningrad Institute of Technology imeni Lensovet

[Abstract] Electron spectroscopy is used to establish the conformation composition of 1,3-alkadienes with various position of the phosphorus atom in the alkadiene chain. It is shown that tert-butyl ester of 2-methyl-1,3-butadiene-1-phosphoric acid (I) has a flat s-trans-conformation, while diethyl ester of 3-chloro-4-methyl-1,3-pentadiene-2-phosphonic acid (II), as a result of steric interactions, has a sloped conformation. The UV spectra of the compounds are analyzed. Thus, the use of UV spectroscopy can establish the conformation composition of phosphorus-containing 1,3-alkadienes with both flat and sloped structure. Reference 1 (Russian).
[295-6508]

REACTIVITY OF ARYLHYDRAZINES IN REACTIONS WITH PHENYLISOCYANATE AND PICRYL CHLORIDE

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNLOGIYA in Russian Vol 26, No 4, Apr 83 (manuscript received 22 Dec 80) pp 398-400

YANCHUK, N. I., Department of Organic Chemistry, Ternopol State Pedagogical Institute imeni Ya. A. Galan

[Abstract] Hydrazine compounds show more reactivity with some substrates than their basicity would indicate through the so-called alpha-effect of nucleophile reaction. The authors conducted quantitative evaluations of this phenomenon in the title reactions in benzene and in water at 25°C. Results showed that monosubstituted hydrazine compounds reacting with phenylisocyanate had the greatest alpha-effect. With reduced electron-donor properties in the substituents in the aromatic nucleus, the alpha-effect declined. The hydrogen atom of the imino-group fulfilled a crucial role in forming the transitional five-membered complex that was essential for the appearance of the alpha-effect, and the nature of both nucleophile and electrophile reagents also were closely tied to the degree of alpha-effect phenomena. References 14: 11 Russian, 1 Ukrainian, 2 Western.
[317-12131]

UDC: 543.4

DETERMINATION OF CERTAIN METALS AS COMPLEX COMPOUNDS BY PHOTOACOUSTIC SPECTROSCOPY

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 38, No 6, Jun 83 (manuscript received 15 Jul 82) pp 965-969

OBREZKOV, O. N., SHPIGUN, O. A. and ZOLOTOV, Yu. A., Moscow State University imeni M. V. Lomonosov

[Abstract] The principle of photoacoustic spectroscopy for analysis of solid and liquid specimens is explained. This work then studies a number of characteristics of the method which determine the possibility of its use for array of metals in the form of complex compounds. Studies were performed using elements in compounds frequently determined by spectrophotometric methods. Absorption spectra of solutions and extracts were recorded with a Hitachi-124 spectrophotometer. PA measurements were made with a Guilford model R-500 photoacoustical spectrometer. The radiation source was a 300 W xenon lamp. The data obtained indicated that the PA signal magnitude changes linearly with a change in concentration of the substance assayed when the incident light was modulated with a frequency above a certain minimum. Quantitative measurements can be performed for the substances selected over a broad range of light-modulation frequencies. However, as specimen thickness or

concentration of the substance being determined increases the concentration, variation of the PA signal in the frequency range near the critical frequency decreases. Analyses were performed on extracts and on aqueous solutions first applied to filter paper or to thin layers of silica gel. The linear section of the calibration graphs $P=f(c)$ are broader than for the spectrophotometric method, the limits of detection significantly lower. The relative standard deviation of the results is 0.03-0.11. Figures 5; references 3: 2 Russian, 1 Western.
[324-6508]

UDC: 543.42:543.51

ANALYSIS OF HIGH PURITY ACIDS BY CHEMICAL-SPECTRAL AND SPARK MASS
SPECTROMETRIC METHODS WITH CONCENTRATION OF IMPURITIES

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 38, No 6, Jun 83
(manuscript received 27 Apr 82) pp 979-983

CHANYsheva, T. A., SHELPakova, I. R., SAPRYKIN, A. I., YANKOVSKAYA, L. M.,
and YUDELEVICH, I. G., Institute of Inorganic Chemistry, Siberian Branch,
USSR Academy of Sciences, Novosibirsk; Novosibirsk State University

[Abstract] The goal of this work was to develop chemical-spectral and spark mass-spectrometric methods of analysis for high purity acids. Specimens were concentrated by evaporation and the question of possible loss of impurities during evaporation is addressed. It is determined that the elements of interest are not lost when solutions of hydrochloric, hydrobromic and nitric acid are evaporated dry in a quartz dish in the presence of graphite powder, if the evaporation rate is not over $0.2 \text{ ml/hr}\cdot\text{cm}^2$. Evaporation was performed in a teflon vessel, which is easier to clean than quartz. Teflon is also not wet by inorganic acids, decreasing the danger of adsorption of impurities by the walls of the dish and assisting in collecting the dry residue after evaporation. In acetic acid, statistically significant losses were found for Sb, Tl, Pt and Au during the process of evaporation. The data indicate that the method selected for evaporation and transfer of the concentrate to the electrode for spark mass-spectrometric analysis introduces no systematic error to the results of determination of 35 specimens in hydrochloric acid and 31 in acetic acid. For nitric and hydrofluoric acids the same results were achieved as for hydrochloric. The limits of detection of 39 elements in nitric, hydrochloric and hydrofluoric acids and 35 in acetic acid by the chemical-spectral method amounted to 10^{-7} - $10^{-10}\%$ of 60 elements, by the spark mass-spectral method it was 10^{-9} - 10^{-12} mass %. References 8: 7 Russian, 1 Western.
[324-6508]

LAYER-BY-LAYER NEUTRON-ACTIVATION DETERMINATION OF PHOSPHORUS AND ANTIMONY IN SILICON STRUCTURES

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 38, No 6, Jun 83
(manuscript received 19 Apr 82) pp 1056-1059

GOL'DSHTEYN, M. M., GIL'BERT, E. N. and YUDELEVICH, I. G., Institute of Inorganic Chemistry, Siberian Branch, USSR Academy of Sciences, Novosibirsk

[Abstract] In layer-by-layer neutron-activation determination of phosphorus and antimony, the substances analyzed together with comparison specimens are irradiated in the thermal channel of a nuclear reactor in a flux of $5 \cdot 10^{12}$ neutrons/(cm²·s) for 5 days in quartz packing. The phosphorus and antimony carriers are introduced to a solution, evaporated to moist salt and transferred to extraction test tubes with 0.2 M sulfuric acid. Ammonium molybdate is added and the molybdophosphoric acid formed is extracted with dioctyl-sulfoxide in toluene, benzene or dichloroethane for 10 minutes. The radio-nucleid extracted from the samples analyzed is identified by determining the half life, which precisely corresponds to the tabular value for ³²P. To confirm the correctness of the method, two halves of the same plates doped separated with phosphorus and antimony were subjected to independent atomic absorption and neutron-activation analysis. Comparison of the profiles of distribution of phosphorus and antimony produced by the two methods show that within the limits of random errors of both methods of analysis there are no statistically significant differences. The limit of detection of the method is found to be $1 \cdot 10^{-10}$ g and $3 \cdot 10^{-12}$ g for phosphorus and antimony; relative standard deviation for use of an oxidation anode and chemical etching is 0.053 and 0.06 for phosphorus, 0.072 and 0.076 for antimony. Figures 5; references 3 (Russian).
[324-6508]

UDC: 543.51

STABILIZING EFFECT OF GLYCERIN ON SECONDARY EMISSION MASS SPECTRA OF BIOORGANIC COMPOUNDS

Moscow KHIMICHESKAYA FIZIKA in Russian No 6, Jun 83
(manuscript received 27 May 82) pp 804-809

TANTSYREV, G. D., POVOLOTSKAYA, M. I. and SARAYEV, V. A., Institute of Chemical Physics, USSR Academy of Sciences, Moscow

[Abstract] A study is made of the stabilizing effect of glycerin on secondary-emission mass spectra of DL-valine. Experiments were performed by bombardment of targets with a beam of Ar atoms at 2.5 keV, intensity about 10^{12} atoms per square centimeter per second, target temperature 25°C. The targets of mixed valine plus glycerine were prepared by adding a known quantity of glycerine to

an aqueous solution of valine (2 mass %). A drop of the water-glycerine solution was applied to a copper substrate and dried in air at room temperature. After the water was removed, a liquid film of a mixture of valine with glycerin 10^{-3} - 10^{-2} g/cm² in thickness was obtained. Mixtures containing 0.006 to 0.992 molar parts valine were studied. It was found that these solutions in glycerine provided high stability of secondary-emission mass spectra and greatly reduced the contamination of the target surface with organic compound molecules present in the residual gases of the instrument. This stabilizing effect is obviously inherent not only for glycerine but for other low volatility fluids in which the substances can be dissolved. Figures 3; references 8: 5 Russian, 3 Western.
[319-6508]

UDC: 543.064:543.426

ATOMIC-FLUORESCENT DETERMINATION OF SELENIUM, ARSENIC AND MERCURY IN ENVIRONMENTAL OBJECTS WITH PRELIMINARY SEPARATION OF DISTILLATE IN A CURRENT OF OXYGEN

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 38, No 6, Jun 83
(manuscript received 16 Mar 81) pp 1060-1065

RIGIN, V. I., Scientific Research and Planning-Design Institute for Mining of Useful Minerals by the Open Method, Krasnoyarsk Division

[Abstract] High temperature distillation of microimpurities in a current of oxygen with subsequent combustion of the distillate in a hydrogen-oxygen flame is used as the basis for selective hybrid determination of selenium, arsenic and mercury in environmental objects such as soil, rock, plant and animal tissues and air with calibration of the atomic fluorescent spectrometer by the use of pure compounds of the elements. The reproducibility and correctness of the method were tested using standard specimens provided by the US National Bureau of Standards. High sensitivity of determination and good reproducibility of results allow the method to be used to estimate the distribution of mercury, arsenic and selenium in individual plant and animal organs and to study the dynamics of accumulation of these elements in the environment. Figure 1; references 16: 6 Russian, 10 Western.
[324-6508]

UDC: 662.74.013.8:628.543.563

EXPERIENCE OF USING AIR LIFT AERATION SYSTEM IN BIOCHEMICAL INSTALLATION

Moscow KOKS I KHIMIYA in Russian No 6, Jun 83 p 52

BRAUN, N. V., DENISOV, A. M., Kemerovo Coke Chemical Plant, PLAKSIN, V. G. and PIMENOV, I. V., Eastern Scientific Research Institute of Coal Chemistry

[Abstract] The productivity of a biochemical installation involving purification of coke chemical production waste water depends greatly on the effectiveness of the aeration system. The authors' institutions have developed an air lift aeration system which provides a coefficient of utilization of the oxygen in the air of 10 to 12%, 3 to 4 times higher than the corresponding figure for previously-used air lift aerators. The productivity of dephenolation of waste water is 60 to 70 m³/hr, 50 to 60% of the total volume of waste water generated at the plant. The operation of the installation during testing yielded the following results: volume of air tank 320 m³, waste water load 30 to 40 m³/hr, compressed gas flow rate 1200-1300 m³/hr. Content of volatile phenols in water before treatment 200-500 mg/l, after treatment less than 1 mg/l. Long-term operation of the system has indicated that it is reliable in operation and its characteristics are stable. The first model of the air lift aeration system has passed state testing and has been recommended for use at biochemical installations in coke chemical production facilities.

[312-6508]

UDC 615.012.6:577.15.062/.066

OPTIMIZATION OF QUASISTATIONARY FERMENTATION PROCESS

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 17, No 5, May 83 (manuscript received 23 Jul 82) pp 584-588

VALUYEV, V. I. and PANOV, D. P., All-Union Scientific Research Institute of Genetics and Selection of Industrial Microorganisms, Moscow; Scientific-Production Association "Promavtomatika", Groznyy

[Abstract] A continuous cultivation process has many advantages over batch processes, but from the technical aspect, problems arise in maintenance of a viable culture and sterility of the enzymatic process. As a compromise, a process was developed with continuous addition of nutrient. Fermentation

begins with a given volume of the medium, gradually adding the nutrient solution containing the necessary nutritional elements; the process is terminated when culture medium reaches a certain final volume. A mathematical model was developed for the biosynthesis of secondary metabolism products. Recommendations were made on the basis of these theoretical considerations and tested in a laboratory using the example of the fermentation of L-lysine. Satisfactory results were obtained, agreeing with theoretically predicted values. Figures 2; references 5: 4 Russian (1 by Western author), 1 Western. [297-7813]

UDC 615.47.03:615.451.014.24

COMPLETE TECHNOLOGICAL EQUIPMENT FOR CONCENTRATION OF SOLUTIONS, RECTIFICATION AND DISTILLATION IN CHEMICAL-PHARMACEUTICAL INDUSTRY

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 17, No 5, May 83 (manuscript received 23 Mar 82) pp 603-610

ZELINSKIY, Yu. G., POPOV, V. V., VOLOGODSKIY, L. B. and MOSKEVICH, E. M., All-Union Scientific Chemical-Pharmaceutical Research Institute imeni S. Ordzhonikidze, Moscow

[Abstract] A number of new instruments has been developed for chemical and pharmaceutical processes. To facilitate concentration of solutions, complex two-stage rotary evaporators have been designed permitting a one-step concentration and evaporation of a solution to dry powder. This type of equipment is useful for thermosensitive products. In the area of fractional distillation the work is going in three directions: design of batch process units for separation of close boiling mixtures at atmospheric pressure, production of continuous and batch distillation equipment for high boiling thermally labile products and development of units which could be used for chemical reactions coupled with distillation of one of the products. Figures 7; references 5 (Russian). [297-7813]

CATALYSIS

NEW SULFURIC ACID CATALYST DEVELOPED

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 11 Jun 83 p 2

[Article by A. Mal'tsev, SOTSIALISTICHESKAYA INDUSTRIYA correspondent, in the column "Industrial Chronicle": "Economical Catalyst"]

[Text] Production of a catalyst that is new in both form and content has started at the testing plant of the "Unipromed" [Ural Copper Industry Scientific Research and Planning Institute]; the catalyst is used to obtain sulfuric acid. Specialists at the enterprise created the new catalyst in cooperation with workers from the Ural Chemistry Scientific Research Institute and workers involved in the production of sulfuric acid from waste gases of copper smelting enterprises.

The catalyst is 20 percent more productive than existing ones, and works twice as long. It is cheaper to manufacture, since used catalysts can be utilized as raw material for the manufacture of new ones, and the outlay of extenders that are in short supply is reduced. The incorporation of this type of catalyst will make it possible to reduce by 15 percent the number of operators and repair workers involved in obtaining sulfuric acid at shops in copper smelting enterprises.

9967

CSO: 1841/293

PHOTOCHEMICAL SYNTHESIS OF 5-SUBSTITUTED PENTACHLOROCYCLOPENTADIENES

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 19, No 5, May 83
(manuscript received 17 May 82) pp 897-915

ZEFIROV, N. S., KIRPICHENOK, M. A. and SHESTAKOVA, T. G., Moscow State University imeni M. V. Lomonosov; Novomoskovskiy Branch, Moscow Institute of Chemical Technology imeni D. I. Mendeleyev

[Abstract] A study was made of the possibility of carrying out photoinitiated radical reactions of hexachlorocyclopentadiene (I). The results are presented from a systematic study of photochemical reactions of hexachlorocyclopentadiene with a broad range of organic compounds. Photolytic reactions of hexachlorocyclopentadiene were generally carried out with incomplete conversion without optimizing the yield of the products in order to estimate the main trends of reaction of hexachlorocyclopentadiene. Usually the photolysis produced multi-component mixtures which, along with trivial reaction products [products of chlorination, pentachlorocyclopentadiene and products of photolysis of the original compound] in all cases contained monosubstituted pentachlorocyclopentadiene as the main product, yielded preparatively with a yield of 5 to 20% and a conversion of 50 to 80%. Photochemical reactions of hexachlorocyclopentadiene can serve as a direct method of synthesis of 5-substituted pentachlorocyclopentadienes. Radical reactions of hexachlorocyclopentadiene leading to monosubstituted pentachlorocyclopentadienes in contrast to halogen methanes occur by a recombination mechanism which is rather selective and sensitive to steric hindrances. Details of all reactions are presented. References 30: 8 Russian, 22 Western.
[299-6508]

CATALYTIC INFLUENCE OF SUBSTITUTED DIPHENYLPHOSPHORIC ACIDS ON COMPLEX ESTER FORMATION

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 19, No 5, May 83
(manuscript received 5 Jan 82) pp 931-935

ZHIL'TSOV, N. P., SEMENYUK, G. V. and KORZHENEVSKAYA, N. G., Institute of Physical-Organic Chemistry and Coal Chemistry, Ukrainian SSR Academy of Sciences, Donetsk

[Abstract] The kinetics of the reaction of butyryl chloride with 1-butenol in toluene at 25°C catalyzed by derivatives of diphenylphosphoric acid were studied. Measurement of the reaction kinetics was performed in a sealed chamber dried with phosphorus pentoxide, since butyryl chloride is significantly hydrolyzed by the moisture in the atmosphere. The course of the process was monitored by chromatographic methods based on the quantity of butyl butyrate formed. In bifunctional catalysis, an increase in the acceptor properties of the substituent in the diphenylphosphoric acid leads to an increase in the capacity for the formation of the hydrogen bond of its electron acceptor center, which should correspond to an increase in catalytic activity, while on the other hand it leads to a decrease in the capability for formation of the hydrogen bond of its electron donor center, which should decrease catalytic activity. As a result of this opposite influence, a change in the nature of substituent does not lead to a significant change in catalytic activity. References 9: 6 Russian, 3 Western.

[299-6508]

UDC 541.128

CATALYTIC PROPERTIES OF NICKEL IN HEXENE-1 SUSPENSION SYNTHESIZED BY PREPARATIVE CRYOCHEMISTRY

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 57, No 6, Jun 83
(manuscript received 17 Mar 82) pp 1557-1559

ZAKURIN, N. V., VASIL'KOV, A. Yu., KOGAN, A. S. and SERGEYEV, V. A., Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow

[Abstract] Details are provided on the cryochemical preparation of nickel in hexene-1 suspension at 77°K under vacuum (10^{-2} Pa), employing a molar ratio of nickel to hexene of 1:100. The final product contained 2 g/liter of nickel. The catalytic activity was investigated at 293°K by following the isomerization of hexene-1 into hexene-2-trans, hexene-2- cis and hexene-3-(trans- and cis-). Conversion of hexene-1 was 77% completed in 4 h and 90% in 50 h. Chromatographic analysis of the products indicated that the transformations rested on a successive migration of the double bond from the α and β position to the γ position. Figures 1; references 7 (Western).

[328-12172]

CATALYTIC INFLUENCE OF DIPHENYLPHOSPHORIC ACID IN THE REACTION OF ESTER FORMATION

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 49, No 6, Jun 83
(manuscript received 21 Dec 81) pp 637-640

SEMENYUK, G. V., ZHIL'TSOV, N. P. and LITVINENKO, L. M., Institute of Physical-Organic Chemistry and Coal Chemistry, Ukrainian SSR Academy of Sciences

[Abstract] Since noncatalytic formation of esters is a multiple-flow process and the intensity of diphenylphosphoric acid catalysis is influenced by alcohol concentration, the kinetics of the reactions were measured at low concentrations of alcohol, allowing the individual rate constants of each parallel reaction stream to be determined. A study was made of the catalytic effect of diphenylphosphoric acid as a function of alcohol concentration over a broad range. Both n-butanol and n-hexanol were used. The high catalytic activity of organophosphorus acids is manifested in the reaction of formation of esters in dilute alcohol solutions and significantly decreased upon transition to concentrated solutions. Figures 3; references 7: 6 Russian, 1 Western.
[322-6508]

CHEMICAL INDUSTRY

NEW CHEMICAL DEVELOPMENTS IN OMSK

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 5 Jun 83 p 2

[Article by E. Chernyshev: "The Effect of Developments"]

[Text] At the All-Union Industrial Carbon Scientific Research Institute in Omsk, a great deal of attention is given to long-range directions in scientific research and to the incorporation of research results in production.

It was here that research was started on obtaining industrial carbon using laboratory equipment and rapid pyrolysis of raw material. At first few people believed that this work would succeed. It was thought that the coking processes would interfere. But those working at the institute disproved this idea. After research, testing, and design operations were carried out at the Omsk industrial carbon plant, which is the base enterprise for the institute, the first equipment based on this new principle was put into operation.

This is also where research was started on the application of low temperature plasma in the production of industrial carbon. After cooperation was established with the USSR Academy of Sciences, those working at the institute created a new industrial process which is now recommended for industrial use. It provides almost complete transformation of the raw material into the final product--industrial carbon--and at the same time reduces to one-fifth or one-sixth of the previous level the amount of waste gases released into the atmosphere.

The institute's associates have incorporated these and other long-range developments recently in a new industrial process and new equipment which can be called the threshold of the plant of the future. There are plans to build and put into operation in 1985 the first such industrial installation with a capacity of 30,000 tons of active industrial carbon "PM-105".

9967

CSO: 1841/293

MONOFILAMENT PRODUCTION

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 12 Jun 83 p 2

[Article by Zh. Tkachenko, SOTSIALISTICHESKAYA INDUSTRIYA correspondent, in the column "Industrial Chronicle": "Monofilaments to Consumers"]

[Text] A shop for the production of monofilaments was put into operation at the Chernigov "Khimvolokno" [Chemical Fibers] Association. Fully automated production lines will make it possible for the chemical workers to put out 500 tons of this product per year. Consumers have already received the first batches of monofilaments produced here.

The association fulfilled ahead of schedule the orders of fishermen and tire workers. An additional 90 tons of synthetic fibers and 140,000 square meters of cord and anide fabric were manufactured for them.

9967

CSO: 1841/293

COAL GASIFICATION

TELEVISION EQUIPMENT INSTALLED AT FACTORY

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 11 Jun 83 p 2

[Article by L. Rybakovskiy in column "Industrial Chronicle": "Television at a Factory"]

[Text] Specialists from the "Yakutugleavtomatika" [Yakutsk Coal Automation Industrial Association] administration installed the first television equipment at the Neryungri Coking Coal Concentrating Factory.

The enterprise is equipped with the latest domestic and foreign equipment, many models of which have still not been put in use throughout the industrial sector. Television control will aid in the improvement of equipment utilization. Industrial television installations will appear in all major sections of production.

9967

CSO: 1841/293

MATERIAL COMPOSITION AND PROPERTIES OF ARTEM IV-A CHEREMKHOVSKIY DEPOSIT FIELD COAL

Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 83
(manuscript received 8 Jul 81) pp 3-7

KRYUKOVA, V. N., KOMAROVA, T. N., BELONOGOVA, L. N., VOLONDZ', F. M. and
KUIIMOVA, N. M., Institute of Petrochemical and Coal Chemical Synthesis,
Irkutsk State University

[Abstract] A study was made of 456 coal samples taken from the Artem IV-A field from 39 boreholes in the deposit. The material composition of the coal was studied by a combination of physical and chemical methods. Chemical and radiographic analysis of ash and solid fractions were used to determine the mineralogic composition of the inorganic portion of the coal. The coal in question is humus-type coal, total thickness of coal seams 2.1 to 6.8 m in the various boreholes (not including rock interlayers). The thickness of the coal seams varies with depth from 0.05 to 1.8 m, deposition depth 11 to 34 m. The coal was found to be similar to ordinary Chermkhovskiy coal though higher in sulfur, 25% of the coal specimens containing over 1.4% S. The coal is moderate in caking properties, similar in semicoking product yield to ordinary Chermkhovskiy coal. In terms of heat of combustion and quality of coal tar produced, the area is in a lower stage of metamorphism than type G Chermkhovskiy coal. The sulfur content varies directly with bisulfide sulfur content. The mineralogic composition of the inorganic portion of the coal and fusion characteristics of the ash were determined: the ash is moderately refractory. The coal is not dangerous for contamination of the environment with lead, arsenic, or mercury. Figure 1; references 8: 7 Russian, 1 Western.
[311-6508]

SOLIDIFICATION POINT AND FLUIDITY LIMIT OF OIL-COAL PASTES AND COAL-HYDROGEN PASTE FORMERS

Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 83
(manuscript received 30 Sep 81) pp 97-100

IL'IN, V. K. and GORSKAYA, T. P., Institute of Fossil Fuels

[Abstract] In petroleum products, coal-hydrogen paste formers and coal pastes based on them, the transition from the liquid to the solid state occurs gradually over a certain temperature interval. The presence of surfactants is very important for determination of the solidification point or range of paraffinous products such as resins and asphaltines. The deviation of calculated solidification point from true solidification point depends on the deviation of calculated viscosity of the mixture of products from the value determined in practice. In this study, several methods were used to determine the solidification point, methods of determining the maximum solidification point of paraffinous products and the Zakharenko melting method, which consists in the determination of the displacement of the level (meniscus) of a tested product in a graduated cylinder as it is melted. The results of the experiments are presented in tabular form. It is found that paste-formers and oil-coal pastes based upon them differ in solidification point by 8 to 12°C for identical specimens depending on the method of heat treatment, which must be considered in long-term storage of these products at low temperatures and their transportation through pipes. Dispersion media and pastes containing large quantities of resins and asphaltines have a broad solidification range. References 7: 6 Russian, 1 Western.
[311-6508]

UDC: 66.096.5

GASIFICATION OF IRSHA-BORODINSKIY COAL IN A FLUIDIZED BED REACTOR

Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 83
(manuscript received 21 Jul 81) pp 119-122

DUBININ, A. M., MUNTS, V. A., BASKAKOV, A. P. and CHOYNZONOV, B. L.,
Ural Polytechnical Institute

[Abstract] The authors have modernized a multichamber gas generator for oxygen-free steam gasification of coal in a fluidized bed described in their previous work. Three processes occur in the device--coking, gasification and the production of heat--in a single cylindrical chamber. Experiments have shown the possibility of oxygen-free steam gasification of coal in a fluidized bed producing products rich in fuel gases. The device is diagramed and described. The composition of the exhaust gas from the gasification chamber, when the reactor is fed semicoke, includes 1.8-4.7% CO₂, 47.1-48.8% CO,

47.5-48.6% H_2 , 0.7-0.8% CH_4 as dry gas, 1.4-4.0 CO_2 , 39.7-39.9% CO , 39.7-39.9% H_2 , 0.6-0.7% CH_4 and 15.8-18.3% H_2O as moist gas. Semicoke is a more reactive material for steam gasification than is coal. Analysis of the data has shown that the installation is usable, requiring no oxygen injection. The gas produced is rich in hydrogen and carbon monoxide and quite suitable for production of methanol or, if carbon dioxide and water vapor is removed, for use in metallurgy for direct reduction of iron. Figures 2; references 3 (Russian).
[311-6508]

UDC: 665.6.032.57.662.76

PROCESSING OF LUMP SHALE WITH LOW HEAT OF COMBUSTION IN GAS GENERATORS

Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 83
(manuscript received 25 Aug 81) pp 123-127

YEFIMOV, V. M., RAAD, Kh. E., DOYLOV, S. K. and SHAGANOV, Yu. V., Scientific Research Institute of Shales, Estonian SSR

[Abstract] The use of fuel shales with low heat of combustion for the production of artificial liquid fuel is very attractive. Practical interest has therefore been expressed in an experiment on the operation of a gas generating station at "Kiviyl" Shale Chemical Plant which has gone on for almost 30 years, processing 25-125 mm lumps of shale with heat of combustion 9.6-10.0 MJ/kg. The history of the plant is briefly described. In 1970-1973, modifications were made to the design of the gas generator at the plant, as a result of which the residual resin content in the solid residue was decreased to 0.5% and steam was no longer required in the process. The heat of combustion of the gas produced was increased from 2.7-3.1 to 3.5-4.0 MJ/m³. By going over to processing of small particle shale and thus increasing the active surface of the layer in preparation of the raw material, using particles of 8 to 10 mm in diameter well sorted from smaller particles with a maximum particle size of 60 to 70 mm the specific surface of the layer can be increased from 50-60 to 120-130 m²/m³ which should produce an equivalent increase in the throughput capacity of the gas generator for shale. Gas generator No. 1 began operating under these conditions in December of 1973 and was easily adjusted to a stable throughput capacity of 230-250 tons of shale per day, a previously unknown level of productivity. All gas generators at the plant were similarly reconstructed in 1974-1977. The throughput capacity of gas generators has now been increased to 190-200 tons of shale per day, the yield of tar from 64-65 to 67-69%. The great increase in shale input has been accompanied by a decrease in the transfer of dust from the vapor-gas mixture, from 15-20 to 3-4% content of mechanical impurities in the heavy resin. The operating life of the installations between cycles of maintenance has also been increased greatly. This and the improved quality of the refractory lining have allowed a decrease in the number of maintenance personnel required by 10%.
Figure 2; references 15 (Russian).
[311-6508]

REMOVAL OF CORROSIVE IMPURITIES FROM WATER WASHING OF OIL IN THE BENZENE DEPARTMENT

Moscow KOKS I KHIMIYA in Russian No 6, Jun 83 pp 31-33

KUZ'MINA, Ye. Ya. and LEBEDEVA, G. N., Eastern Scientific Research Institute of Coal Chemistry

[Abstract] To determine the possibility of removal of corrosive impurities from absorption oil by water, the authors determined the distribution coefficients of oil-absorbed gases and products of their interaction between oil and water. An equation for determining the distribution coefficient of volatile substances between two immiscible fluids was used to calculate $r_{o/w}$ for HCN, H_2S and NH_3 , using the distribution coefficients of these substances between the gas phase and oil and between the gas phase and water. The following substances were used in the study: absorbing petroleum boiling in the 210-295°C range, the same oil purified under production conditions by sulfuric acid to remove bases to a residual content of 0.7% as opposed to the original content of 9.7%, and the lightest component of the oil--benzene of analytic purity, as well as the most active component--quinoline, standard absorptive solar oil, light catalytic cracking gas oil, promising for use as an absorbing oil, ammonium thiocyanate, ammonium cyanide and a solution of hydrogen cyanide obtained by dissolution of yellow potassium ferrocyanide. Experimental determination of distribution factors was performed at 22-28°C in a separatory funnel with a mixture of oil and water in a mechanical vibrator at 120 oscillations per minute for 4.5 minutes (three sessions of 1.5 minute each with interruptions of 0.5 minutes) per experiment. It was found that as the water to organic fluid ratio changed from 1:1 to 1:10 the distribution factor remained practically unchanged. The calculated and experimental data were found to agree closely. Ammonia dissolves most poorly in the oils. Hydrogen cyanide is significantly less soluble in the oils than in water, except in quinoline. The solubility of ammonium cyanide is 10 times greater in oil than in water, ammonium thiocyanate 60 times greater. Water washing can thus not be considered an effective means of removing corrosive substances from oil. References 7 (Russian). [312-6508]

UDC: 538.6(661.522.2+662.749.33)

USE OF MAGNETIC TREATMENT TO INTENSIFY PROCESSING OF CERTAIN CHEMICAL COKING PRODUCTS

Moscow KOKS I KHIMIYA in Russian No 6, Jun 83 pp 33-35

GLUSHCHENKO, I. M. and GRISHAYENKO, S. P., Dneprodzerzhinsk Industrial Institute

[Abstract] Magnetic treatment of aqueous systems has become an important factor in improving many technological processes. The Department of Chemical Technology of Solid Fuels of the authors' institute has for many years studied

the use of magnetic fields in coke chemical processes and the design of magnetic apparatus. Work has been performed in the following three main directions: 1) creation of relatively simple, safe and productive apparatus; 2) intensification of heat exchange processes in chemical shops by elimination of deposition of hardness salts on heat exchange apparatus; and 3) intensification of technological processes to increase productivity and improve product quality. Examples of all three areas are briefly cited. The results of the studies indicate that magnetic processing is a quite realistic and effective factor in intensifying certain technological processes in the coke chemical industry. The mechanism of action of a magnetic field requires further theoretical study.
[312-6508]

UDC 622.831.32 + 541.183.5

CHANGES OF MECHANICAL PROPERTIES OF ANTHRACITE DUE TO ADSORPTION OF GASES UNDER PRESSURE

Moscow KOLLOIDNYY ZHURNAL in Russian Vol 45, No 3, May-Jun 83
(manuscript received 10 Feb 82) pp 410-415

VINOKUROVA, Ye. B. and KETSLAKH, A. I., Moscow Mining Institute

[Abstract] The goal of this study was to investigate the effect of adsorbed gases at elevated pressures on anthracite under tension. Because mined coal shows chemical and structural properties changing from sample to sample, two brands of graphite were studied: a porous graphite PG-50 resembling anthracite by its mechanical properties and MPG-6, a stronger graphite with low porosity. No substantive changes were observed in these samples in an atmosphere of inert gas and in nitrogen, which is poorly adsorbed at room temperature. Repeated saturation of anthracite with methane under high pressure, coupled with rapid degasification led to a lower modulus of elasticity. Carbon dioxide proved to be an adsorption active medium for anthracite: its samples removed from the test chamber disintegrated by manual compression. Carbon dioxide then was shown to cause the greatest effect on mechanical properties of anthracites. Figures 2; references 18: 15 Russian, 3 Western (1 by Russian authors).
[296-7813]

STUDY OF GAS COAL CONVERSION PRODUCTS DURING THEIR STEPWISE PULVERIZATION

Moscow KOLLOIDNYY ZHURNAL in Russian Vol 45, No 3, May-Jun 83
(manuscript received 23 Dec 81) pp 605-607

KHRENKOVA, T. M., KIRDA, V. S. and DUBROVA, S. N., Institute of Combustible Minerals

[Abstract] During pulverization of coal in vibrational mills, chemical changes take place in its organic mass caused by mechanical destruction. Physical and chemical properties of dispersed samples and samples dissolved in various organic solvents were studied after their pulverization. A stepwise mechanical destruction method was used. All soluble products were extracted from the starting material; then it was finely ground in a vibro mill. Again it was extracted and repulverized two more times. It was shown that changes in the content of active acid groups were directly related to increase in phenolic hydroxides. Oxygen content dropped 2.6 fold from the crude phase to the III-step grinding. The dissolved fractions showed increased content of aromatic structures with lower aliphatic and alicyclic fragments. During step-wise pulverization in air, oxidation processes occurred along the C-O-C, C-C and C-H bonds leading to formation of new soluble products. References 4:
3 Russian, 1 Western.
[296-7813]

ELECTROCHEMISTRY

UNUSUAL CRYSTALS

Moscow **TEKNIKA I NAUKA** in Russian No 5, May 83 pp 27-29

[Report of V. Belyakov, doctor of physical and mathematical sciences, at the All-Union Conference Seminar on Non-Classical Crystals held in Armenia at the end of 1982]

[Text] "We find crystals everywhere. We walk on crystals, we build things of crystals, we process crystals at factories, we grow crystals in laboratories and in factory devices, we use crystals broadly in technology and science, we find crystals in living organisms, we dig into the secrets of crystal structure, we enter outer space with the aid of instruments using crystals and we grow crystals in space laboratories." Thus wrote the well-known Soviet crystallographer Marianna Shaskol'skaya in the book "Crystals."

The word crystal is unavoidably associated with something hard, of regular form with many facets. It can be a little crystal of ice or table salt, quartz or a diamond. For scientists who study problems of solid state physics, however, such classic crystals do not provide much of interest. They are currently asking more complex questions, such as consideration of one- or two-dimensional crystals, or current thinking about four-dimensional crystals. They wonder how to explain a substance that is at a temperature close to absolute zero that remains a liquid, yet shows some of the characteristic properties of crystals. In a word, so-called "non-classical" crystals are in the forefront of attention. We have already written about liquid crystals for the readers of **TEKNIKA I NAUKA** twice (1979 No 1 and 1982 No 4), describing typical representatives of the non-classical crystal "family."

At the end of 1982, a major All-Union Conference Seminar on Non-Classical Crystals was held in Armenia. V. Belyakov, doctor of physical and mathematical sciences, discusses certain properties and interesting aspects of practical utilization of such crystals. [His report follows.]

Study of non-classical crystals is already at the stage where fully practical ways of putting them into practical applications are at hand. They can provide the increased reliability and low cost for various products and make essential miniaturization possible. More than that, we can confidently predict the creation of new technological processes and the development of materials with properties that science fiction writers have not even dreamed of.

Since the scope of this article will not permit me to tell of all these developments, I will limit my report to just a few directions of potential use for these unusual substances.

A Crystal in a Crystal

The atoms of one substance can be imbedded in the crystalline structure of another, either replacing atoms of the latter in the matrix or fitting into its voids. Hydrogen atoms readily imbed into the crystalline matrices of many transitional metals, forming unique metal-hydrogen systems. In contrast, however, to most substances, the hydrogen in such a system does not "behave according to the rules" as we know them. Either its atoms form their own crystal within the metal crystals with which they have combined, or they behave like a liquid, or else they acquire the properties of a gas. More than that: depending on pressure and temperature, the hydrogen crystals that form can undergo phase transformations, i.e., they can go from one crystalline modification to another. This hydrogen behavioral pattern in itself is extremely interesting and serves as the subject of intense study. Yet even more impressive is the behavior of hydrogen atoms when a metal-hydrogen system is cooled.

According to classical notions, reducing temperature brings with it a weakening of the thermal movement of atoms and reduction in their diffusion. More than that, at absolute zero the thermal mobility and diffusion of atoms should cease completely.

Researchers have determined, however, that hydrogen does not want to submit to these principles. At reduced temperatures, the movement of its atoms does not slow down very much, and at a temperature approaching absolute zero (1 K and below), they not only do not become still, but begin to diffuse even more intensively than previously. It became necessary to admit that hydrogen atoms cease to submit to the laws of classical mechanics.

The Pathway to Superconductivity

For half a century already, scientists have been breaking their spears in considering this problem. One suggested variant proposes using super-high pressure to obtain metallic hydrogen, then use it to produce high-temperature superconductivity.

That is where the paths cross for such super-conductive hydrogen and the anomalies found in hydrogen's behavior in metals.

The current level of science and technology makes it possible to create pressure of the order of a megabar. That means that there is hope that gaseous hydrogen can be compressed to the point of the formation of its metallic phase. The task, however, is to obtain not just a phase with metallic conductivity, but a metastable phase, i.e., one that will maintain its conductivity after pressure is released. So far not even the metallic hydrogen phase, let alone its metastable phase, have been produced by anyone.

But hydrogen imbedded in the crystalline matrix of a metal is what is needed. The way to achieve it is first to produce a high concentration of hydrogen atoms in the metal matrix. This can be done by heating a piece of metal to high temperature in a hydrogen atmosphere and maintain the conditions for a sufficient time period.

As a result of diffusion, a multitude of hydrogen atoms penetrate the metal matrix and a high concentration develops that is preserved after the metal is cooled. The distance between the imbedded hydrogen atoms positioned in the building blocks or the inter-block spaces of the metal's crystalline structure is much smaller than in the gaseous phase. In effect, this phenomenon is the equivalent of exerting external high pressure on the gas. Thus we obtain the analogue of metallic hydrogen.

Experiments have shown that a metastable hydrogen condition can also be obtained in the metal matrix. For that reason, scientists consider this route to be promising for obtaining not only superconductivity, but also high-temperature superconductivity.

Hydrogen as a Fuel. How to Store it

No less important than superconductivity is the problem of hydrogen-energy production, or the use of hydrogen as a fuel for internal combustion engines, turbines, etc. There are already automobiles using hydrogen as fuel, but we are a long way from mass use of "hydrogen" engines, and there are many obstacles along the route. One of the most formidable is the problem of storage and transport of hydrogen fuel.

Actually, if we recognize that enormous amounts of hydrogen can be dissolved in some metals, and that hydrogen's ability to be imbedded in a bound state in a metal depends on temperature and pressure, then one solution might look like the following: A metal, such as zirconium, could be saturated with hydrogen under high temperature and pressure, and then the temperature and pressure could be reduced to normal values. As a result, the hydrogen would be "locked" into the metal structure, with extremely high density. And there you have a reservoir for hydrogen! Furthermore, no external pressure would be necessary to maintain this extreme density. The hydrogen could be extracted from the metal simply by raising the temperature slightly, at which the atoms would begin to leave the metal matrix. Such an excellent solution is fully realizable.

A metal-hydrogen system offers hope for realizing a very original approach for transporting hydrogen fuel to the engine without using tubing. If external effects can make it possible to move the hydrogen atoms in the metal matrix in a determined direction, that could be a method to transmit the hydrogen for some distance along the conduits.

The fact that such a transport system is completely possible is under no doubt. You will find out how it can be implemented a little later.

Solid Electrolytes

There is an unusual, little-known class of substances with unique properties. They are called super-ion conductors, or solid electrolytes.

You will recall that the electrical conductivity of solid bodies is determined by their electronic structure, and that electrolyte fusions have ion conductivity. It would seem to follow simply that if electrical conductivity is observed we are dealing with a solid substance, and if we have ion conductivity, then we have either a liquid or a fusion. It turns out, however, that there are substances that do not fit that criterion. The substances in question are solid like all

crystals, resilient and mechanically durable. At the same time, at a temperature far from the melting point, they possess ion conductivity that is close to the conductivity of a fusion, and at times even surpasses it. These are the substances that have been labelled super-ion conductors.

An example of a typical super-ion conductor is the compound Ag_4RbI_5 . It has ion conductivity even at room temperature, and that conductivity is greater by a factor of 10^{18} than that of table salt at the same temperature. That is remarkable! Here conductivity is originated not by light electrons, as in metals, but by silver ions that are hundreds of times heavier.

Where is such an enormous number of free ions to be found in a solid substance? In order to understand the physical nature of ion conductivity, you must remember that the ion crystal can be considered ideal in the strict sense of that word only at a temperature of absolute zero. With increasing temperature, part of the ions are necessarily thrown off the crystal matrix blocks as a result of thermal excitement. They enter the space between the matrix blocks. The remaining block of a crystalline matrix, that part that is not taken up by the ion, has been conventionally labelled the "vacancy." Thus in a crystal at a temperature other than absolute zero, there are always ions in the inter-block space and the vacancy. When an electrical charge is applied to the crystal, these ions can migrate from one position to another, creating a current in the ion crystal. In this phenomenon the strength of the current is directly proportional to the number of vacancies or of ions in the inter-block spaces.

In most examples of ionic crystals, the number of vacancies and inter-block spaces is small relative to the number of blocks in the matrix. As a result only a very low ion conductivity is present, even in comparison to semiconductors. In compounds regarded as super-ionic, there is a different situation. With increased temperature and attainment of its maximum value, the number of vacancies and ions in the inter-block spaces grow like an avalanche, becoming fully comparable to the number of blocks in the crystal matrix. This is the reason why the conductivity of a solid electrolyte turns out to be so high that it can surpass the conductivity of fusions and semiconductors.

Here we should note immediately that the rapid increase in the number of vacancies and ions in the inter-block spaces relates only to one type of ions. The other ions of a given substance remain in their places. There is sort of a melting of the matrix formed of ions of a single type, while within the matrix of remaining ions a fluid of ions of the melted sub-matrix forms. For example, in the Ag_4RbI_5 compound, the matrix formed of Rb and I ions contains a liquid of ions of Ag^+ silver. Thus the presence of anomalously high ion conductivity in super-ion conductors is tied to the melting of the ion matrix of a certain type along with the preservation of the matrix formed of different ions in the crystal.

So far we have been discussing inorganic crystalline compounds. The properties of super-ion conductors can, however, be found in some glass-like and even organic polymer substances.

Scientists have been able to obtain solid crystalline compounds with high proton conductivity, i. e., compounds wherein charge transfer is effected by hydrogen ions. Now let us turn to the problems of hydrogen transport.

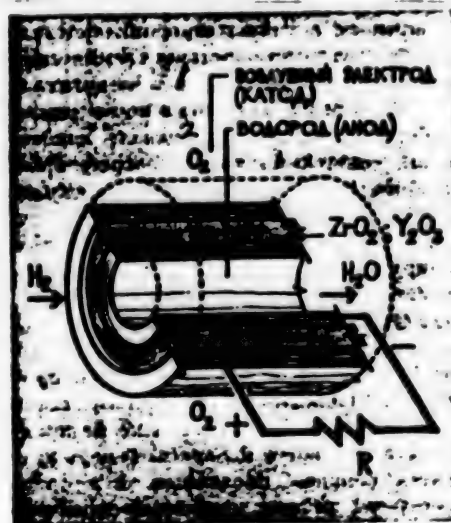
Figures:

Schematic diagram of an electrical battery with solid electrolyte

Key: 1. beta alumina
2. liquid sodium
3. Sulfur fusion

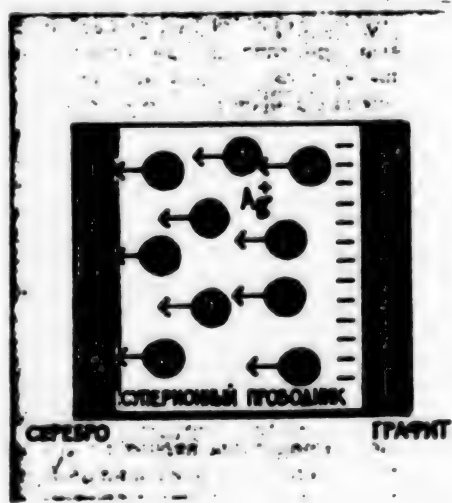


Schematic diagram of fuel element
Key: 1. "air electrode" (cathode)
2. Hydrogen (anode)

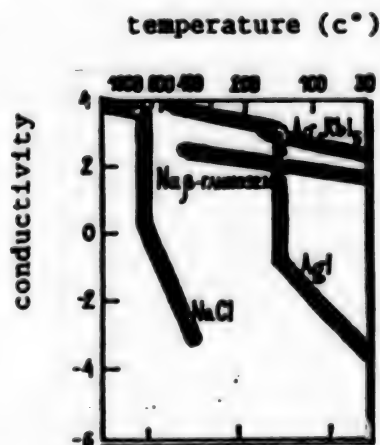


Electrochemical cell with graphite and silver electrodes

Key: 1. Super-ion conductor
2. Silver
3. Graphite



Electrical conductivity of several ion crystals. The leap in conductivity of table salt, for example, is caused by melting.
Key: 1. beta-alumina



Let us take, for example, the compounds KHF_2 and KH_2PO_4 . In them the charge is carried by the H^+ hydrogen ions. That means that the electrical current in these substances is in the form of a flow of hydrogen atoms, or more precisely, hydrogen ions. This leads to the possibility of creating conduits from such materials and transporting hydrogen with them. It is sufficient to establish a normal difference in potential at either end of the conduit, so that the flow of hydrogen atoms will move along it.

Batteries and Fuel Elements

Doubtless the reader is expecting practical applications of these discoveries that scientists have developed. Well, here are some examples.

One of the best known and most effective application of super-ion conductors is their use as electrolytes in electrical batteries. Let us return to the already discussed compound Ag_4RbI_5 . A battery made from it is durable and will function in a temperature range of -55 to $+75^\circ\text{C}$, and it can provide a steady current for long periods, even years. Such batteries have been produced and have passed use tests. During operation, a transformation of chemical energy from the reaction of silver and iodine atoms makes electrical energy.

In another design, batteries use the super-ion conductor beta-alumina as an electrolyte, and liquid sodium and a sulfur fusion as electrodes. Hence this is a sodium-sulfur battery. Its advantage is record capacity, with every kilogram of mass producing 200-300 watts, and electrical capacity of up to 300 KWH. Here in the solid beta-alumina electrolyte, the current is carried by Na^+ sodium ions. The great advantage of the sodium-sulfur battery is its charging capacity. If a discharged battery of this type is subjected to an electrical current in the opposite direction it becomes suitable for re-use as a battery. The number of such recharges can reach several hundred.

There is a possibility of using super-ion conductors in fuel elements as well, whereas, in batteries, chemical energy is converted into electrical energy. One of the drawings shows a schematic drawing of a high-temperature fuel element in which the electrolyte is a solid solution containing zirconium and yttrium-- $\text{ZrO}_2\text{-Y}_2\text{O}_3$. In this cell direct transformation of chemical energy into electrical energy is achieved much more effectively in principle than the production of electrical energy in the turbine-generator system usually employed.

A Dependable Heater and Much More

Super-ion conductors can also be used to make high-temperature heating elements that can work in oxygen-containing atmospheres, i.e., under conditions that preclude prolonged use of usual high-temperature devices such as incandescent light filaments. In this area, super-ion conductors with ion conductivity based on oxygen ions have been proven to be useful. Thus a heating element based on $\text{ZrO}_2\text{-CaO}$ can provide temperatures up to $2,200^\circ\text{C}$ when working in air. In addition, the greater the oxygen content in the surrounding atmosphere, the better such an element works.

The dependence of several properties of solid electrolytes on the environmental composition (such as the oxygen concentration in the example given above) can be used to create sensors to measure the content of various gases in the surrounding atmosphere. Analyzers have already been made based on that principle to determine content of gaseous oxygen, sulfur, fluorine, hydrogen, carbon dioxide and methane. Here it is important to note that the gas content is determined on the basis of changes in the electrical characteristics of a chain containing a solid electrolyte,

and that is the most effective form for transforming and processing the information collected. It is particularly promising to employ such sensors to maintain optimum fuel use in automobile engines, simultaneously reducing fuel consumption and the emission of harmful impurities in exhaust gases into the atmosphere.

Lacking the possibility to tell of many other areas for using super-ion conductors, such as information processing systems and medicine, I will conclude my remarks with an original example. I am talking about the possibility of precise balancing of a body's center of gravity at the atomic level. The idea is to use mass transfer related to the ion flow. Actually, since in super-ion conductors the flow is ion movement, with its aid it is possible to regulate shift in the center of gravity of the conductor. In one direction of flow that center of gravity will move in one direction, while with the reverse current the balance will shift. Knowing the mass of ions that carry the current, it is simple to figure the amount of electricity that needs to be transmitted through the system to move its center of gravity by a given amount.

The above examples show some of the possibilities of non-classical crystals. Who knows, what new practical applications will be found by scientists and put into concrete devices by engineers. That is an inexhaustible source of new ideas and creative invention.

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12131

CSO: 1841/304

UDC: 547.738.088.8

HIGHLY CONDUCTIVE TETRASELENOTETRACENE COMPLEXES WITH TETRACHLORO- AND
TETRABROMODIPHENOQUINONES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 5, May 83
(manuscript received 29 Jan 82) pp 1127-1131

STARODUB, V. A., GLUZMAN, Ye. M. and GOLOVKINA, I. F., Kharkov State
University imeni A. M. Gor'kiy

[Abstract] The authors recently produced complexes of tetrathiotetracene with tetrachloro- and tetrabromodiphenquinones in a ratio of 1:2. With this stoichiometry it is possible to interact neutral and ion-radical forms of the acceptor (so-called wandering aromaticity) which probably results from the comparatively high conductivity of these complexes for tableted specimens. The author studied complexes of tetraselenotetracene with tetrachlorodiphenquinone and tetrabromodiphenquinone which have the composition 2:3. The IR spectra contain intensive absorption bands of tetrachlorodiphenquinone and tetrabromodiphenquinone anion radicals at 1240 cm^{-1} and a singlet band at 800 cm^{-1} instead of the triplet band in the spectrum of neutral compounds, as well as other differences. These specifics of the spectrum are typical for highly conductive quasi-unidimensional ion radical salt crystals. IR spectroscopic analysis thus gives reason to believe that the complexes are highly conductive. Conductivity measurements performed on tableted specimens confirm this assumption. Figure 1; references 12: 5 Russian, 7 Western.
[295-6508]

UDC 541.13

TEMPERATURE DEPENDENCE OF ELECTRIC CONDUCTIVITY OF HIGH-RESISTANCE ORGANIC
LIQUIDS

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 57, No 6, Jun 83
(manuscript received 23 Mar 82) pp 1561-1563

KOPYLOV, Yu. A., Dnepropetrovsk Agricultural Institute

[Abstract] Mathematical treatment was accorded to the determination of the temperature dependence of dielectric and semiconductor organic liquids. The

calculations demonstrated that, in general, current flow must be evaluated in terms of a complex of activation parameters which can only be derived from a joint determination of the temperature and voltampere characteristics that allow for differentiation of activation processes at the level of 0.4 eV or less. The temperature dependence of the current density (but not of electric conductivity) is best expressed by $\ln j = f(1/kT)$, where j = current density, k = Boltzmann constant, and T is the temperature. Figures 2; references 6 (Russian).
[328-12172]

FERTILIZERS

NEW PHOSPHORUS PROCESSING TECHNIQUES

Leningrad LENINGRADSKAYA PRAVDA in Russian 27 May 83 p 1

[Article by Yu. Vorob'yevskiy: "Using New Technology"]

[Text] The successful development of a new processing method for concentrating poor ores at the "Fosforit" [Phosphorite] Association represents a major gift in honor of Chemists' Day.

Today here at the experimental industrial installation testing is being carried out on methods of processing phosphates from the Kazakh deposit in Karatau.

They contain from one-half to one-third the amount of useful components found in the Kola apatites, from which 80 percent of the country's fertilizers are produced. The growing agricultural demand for fertilizers requires intensified production of this product. At the same time, the beds of the rich raw materials are being exhausted. There are plans to apply the new processing method, the efficiency of which has been confirmed in Kingisepp, to ores from deposits in Kazakhstan and Estonia.

9967

CSO: 1841/293

PROBLEMS AT DZHAMBUL SUPERPHOSPHATE PLANT

Moscow EKONOMICHESKAYA GAZETA in Russian No 20, May 83 p 4

[Article by Ye. Kozlov, EKONOMICHESKAYA GAZETA correspondent: "Unjustified Difficulties"]

[Text] The Dzhambul Superphosphate Plant fulfilled its plan for four months according to all indicators. There were additional production sales of over 2 million rubles. This would be very gratifying, if not for one condition. The delivery of mineral fertilizers to remote regions of the country is reaching only 60 percent of the level agreed upon.

Fertilizers are sent to these regions in soft containers that are used just one time. The "Soyuzplastpererabotka" Manufacture of Plastics and Chemical Containers Industry Association of the Ministry of the Chemical Industry is supposed to provide the plant with these containers. In December of last year the Dzhambul workers received a notice signed by V. Dergausov, chief of the Association's supply section, that the enterprise had been allocated 22,000 containers; a specific supplier was named--the varnish and paint plant in the city of Gulyaypole in Zaporozhye Oblast.

This news caused some alarm in Dzhambul: over 33,000 containers are needed for the annual production plan. But this was not the only problem. The fertilizers need to be sent to northern regions during the spring and summer navigation periods. Therefore the demand for containers in the first quarter accounts for almost 15,000 of the total, and the plan was to supply only 5,500 during that period.

For almost the entire first quarter the Superphosphate Plant sent messengers to the Ministry of the Chemical Industry, USSR Gossnab, and other organizations to prove that without the soft containers, the plan for delivery of mineral fertilizers to remote northern regions could not be fulfilled. They finally were successful in proving this. Recently "Soyuzplastpererabotka" allocated the full number of containers needed by the plant for the half-year (since the first quarter has already passed, at issue actually is the second quarter). Now rush work is starting at Dzhambul. This is absolutely necessary if the agreed upon deliveries are to be made on time.

So this situation will not be repeated, it is necessary now to guarantee delivery of the containers for the second half of the year.

IMPROVEMENT OF KAZAKH MINING INDUSTRY SUGGESTED

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 2 Jun 83 p 2

[Article by B. Miletskiy, general director of the "Zapkarzgeologiya" (Western Kazakh Geology) Association, and winner of the USSR State Prize: "A Specific Program for a Complex"]

[Text] Fifty years ago at a tiny railroad station in the uninhabited Kazakh steppe, where there was no electrical power and no water, a group of enthusiasts descended from the train. In a record-making short period of time, the champion of the republic's chemical industry was erected--the Aktyubinsk Chemical Plant imeni S. M. Kirov.

The construction site for what was a large plant for that time was not chosen by accident, of course. Phosphate deposits had been found in the area, which were meant to serve as a base for the production of mineral fertilizers. But the plant will soon observe its fiftieth anniversary jubilee and all these years the enterprise has been bringing in phosphate concentrate from 3000 km away, from the Kola Peninsula. And the ores lying virtually at the plant's doorstep have remained untouched.

All this can be easily explained. In those years long ago, geologists discovered only small sections of phosphorite deposits. They thought that there would not be enough to supply the plant that was being built. But soon the rich Khibinsk apatite beds were discovered, and development of the Aktyubinsk deposits seemed economically unprofitable in comparison.

Now, many years later, a new generation of geologists has proved that the phosphorite beds discovered earlier with stores of 20-40 million tons of ore are just small and unrepresentative fragments of the vast Aktyubinsk phosphorite basin, the reserves of which in the central region alone are estimated confidently at 3 billion tons.

The collective of the "Zapkarzgeologiya" Association, under the direction of Academician A. Yashin, conducted thorough, systematic geological research on the phosphorite deposits located in the Aktyubinsk Ural region; this research made it possible not only to make a long-range evaluation of the new phosphorite basin in the USSR, but to prepare completely for the industrial development of the Chilisay deposit. On the basis of this, the third largest

raw materials base for the extraction and processing of phosphates in the country is now being created.

Work started at the initiative of the Aktyubinsk obkom of the Communist Party of the Kazakh SSR on the exploration of the Chilisay deposit was carried out in a very short period of time and with a great economic effect. Moscow scientists provided the basis for obtaining high quality phosphorite concentrate from the relatively poor Aktyubinsk ores, suitable for reprocessing into ammo-phos and other concentrated mineral fertilizers. The Chilisay deposit was determined to be one of the largest in our country according to the reserves that were explored. Due to the easy mining conditions--the phosphorite layer is located practically on the surface--and a number of other preconditions, a ton of the Chilisay phosphate is 30 percent cheaper than a ton of the well-known Karatau phosphoric anhydride. In accordance with the "Basic Directions for the Economic and Social Development of the USSR for 1981-1985 and up to the Year 1990", approved by the 26th CPSU Congress, there are plans to put into operation in 1985 the first stage of the Chilisay Mining and Concentrating Combine.

The Ministry for the Production of Mineral Fertilizers has decided that the Chilisay concentrate will be used not only for the production of complex concentrated mineral fertilizers, but also for production of phosphorite meal. When the Chilisay Mining and Concentrating Combine is put into operation at full capacity, almost three-fourths of this valuable concentrate will be used for the production of phosphorite meal.

Here we, the geologists, are not in agreement with the chemists. We do not consider these plans to be optimal. The point is that we have made preliminary explorations of three more phosphorite sites in the central area of the Aktyubinsk basin--the Pokrov, Algin, and Bogdanov sites. The ores from the first two deposits are much more preferable for the production of phosphorite meal than the ore from the Chilisay site. These deposits contain large reserves characterized by a stable phosphoric anhydride content, compact ore beds, and favorable mining conditions. But in comparison with the Chilisay ore, these ores have an elevated carbonate level, and therefore it would be more rational to use them in the production of phosphorite meal. An elevated carbonate content in this case only improves the quality of the product.

Unfortunately, the Ministry for the Production of Mineral Fertilizers did not support our suggestions for detailed exploration of the Algin and Pokrov deposits. After the Chilisay project, the chemists are planning to build a second mining enterprise on the base of the Bogdanov group of deposits, the ores of which are like the Chilisay ores and have a low carbonate content. They are more suitable for processing into complex fertilizers not only in terms of their composition, but also because they do not require the additional operation of calcination.

Therefore we recommend and believe that it would be advisable for the Ministry for the Production of Mineral Fertilizers and the USSR Ministry of Geology to conduct an in-depth comparative analysis of all three deposits. This would help, on the basis of technical and economic calculations, to make a sound choice for the optimal construction of a new mining and chemical enterprise in

Aktyubinsk Oblast. With regard to geological explorations, our collective can do this work in a very short period of time, and it will not require large additional sums of money.

Incidentally, the geological research being conducted by the "Zapkazgeologiya" Association for the development of a raw materials base for the production of mineral fertilizers is not limited to the area of the Aktyubinsk phosphorite basin. Western Kazakhstan is the only region in the country where significant reserves of boron and potassium salts have been discovered alongside large phosphate reserves; these include chloride-free sulfate potassium salts, gypsum, and several other so-called agricultural ores.

In the 11th Five-Year Plan our association is planning to expand the raw materials base of boric ores in Western Kazakhstan. The success of this work can ensure a significant increase in the production of one of the micro-fertilizers that is in short supply.

The importance of chloride-free sulfate potassium salts in increasing the yield of industrial crops is widely known. Large reserves of this raw material are concentrated in the Zhilyansk deposit that is also close to the city of Aktyubinsk. The Leningard Halurgy Institute has proved that effective complex fertilizers can be obtained from this raw material. In this connection it would be advisable to speed up the work on the technological study and exploration of the Zhilyansk deposit. We believe that this should be reflected in the plans of the Ministry for the Production of Mineral Fertilizers and the USSR Ministry of Geology in 1984.

It is also appropriate here to note that Western Kazakhstan contains immense gypsum reserves for improving soils with high salinity. Significant reserves of this raw material are concentrated in particular in the Indersk salt dome structures in Guryev Oblast, and in the residues of exhausted deposits. But the Indersk gypsum is still not being utilized, as is the case with the Aktyubinsk gypsum deposits that have been explored.

All this leads to the conclusion that there is an immediate need to work out a special, directed program for the development of the unique raw materials resources of Western Kazakhstan. On the basis of these resources it is completely possible to create a major complex for the production of mineral fertilizers, micro-fertilizers, and means for chemical reclamation of soils. This corresponds completely to the interests of realizing the USSR Food Program.

9967

CSO: 1841/293

FREE RADICALS

UDC: 547.234+541.60+547.339.3

N-NITRENES, PART 1: FORMATION OF FREE RADICALS IN DECOMPOSITION OF DIBENZYL-AMINONITRENE

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 19, No 5, May 83
(manuscript received 15 Mar 82) pp 977-981

SAVIN, V. I., MOROZOV, V. I. and KITAYEV, Yu. P.

[Abstract] Results are presented from a study of the reaction of decomposition of dibenzylaminonitrene using the method of spin traps. In comparison with simple alkyl radicals, the benzyl radical is a resonant stabilized radical. The stabilization energy is 13 kcal/mol. However, the benzyl radical cannot be considered stable. Its lifetime in solution is a small fraction of a second. Of the great selection of reactions leading to dibenzylaminonitrene, the authors selected thermal decomposition of sulfoacid hydrazides, the reaction between N, N-dibenzylhydrazine and p-nitrobenzenesulfochloride and the oxidation of N, N-dibenzylhydrazinebimercurictrifluoroacetate. The results indicated that the decomposition of dibenzylaminonitrene occurs through a stage involving the formation of benzyl radicals. One molecule of dibenzylaminonitrene yields two benzyl radicals. The reaction of the pair of benzyl radicals leads to an end product--dibenzyl. Some of the benzyl radicals go into solution where, meeting a spin trap, they react to form nitroxyl. Figure 1; references 26: 3 Russian, 23 Western.
[299-6508]

UDC: 541.64:541.14

FORMATION OF RADICAL PAIRS UPON INTERACTION OF DIPHENYLMETHYLENE IN TRIPLET STATE WITH POLYMETHYLMETHACRYLATE

Moscow KHIMICHESKAYA FIZIKA in Russian No 6, Jun 83
(manuscript received 12 May 82) pp 818-822

VOROTNIKOV, A. P., DAVYDOV, Ye. Ya., PARIYSKIY, G. B. and TOPTYGIN, D. Ya.,
Institute of Chemical Physics, USSR Academy of Sciences, Moscow

[Abstract] A study is presented of the regularities of the reaction of carbenes in polymers. In this work the transformation of diphenylmethylen (I) obtained by photodecomposition of diphenyldiazomethane (II) to polymethylmethacrylate (III) was studied. The base state of the diphenylmethylen was

the triplet state. It is therefore a convenient object for EPR method study. The experiments utilized a film of III 50 μm thick with the addition of 0.1-0.5 M of II. Many experiments utilized specimens prepared by application of (II) and (III) on silica gel from a solution in methylene chloride. Irradiation of the films at 77 K with light absorbed by the additive leads to the formation of (I) in the triplet state. EPR and UV spectra agree with data from the literature. The data indicate that the overwhelming portion of macroradicals of (III) formed under these conditions have the structure of (IIIa) $(\text{CH}_2-\text{C}(\text{CH}_3)(\text{COOCH}_2)-\text{CH}_2)$. Kinetic data are discussed. For the first time the fact of formation of radical pairs in the process of conversion of diphenylmethylene in the triplet state to a solid polymer matrix is established. The kinetic data show that the thermal death of (I) in (III) occurs as a result of transfer of an atom of hydrogen by a tunnel mechanism. This can lead to the formation of products of insertion of carbene into the macromolecules. Figures 3; references 10: 9 Russian, 1 Western.

[319-6508]

MIXED NEODYMIUM AND URANIUM SELENIDES

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 28, No 6, Jun 83
(manuscript received 23 Apr 82) pp 1388-1390

SLOVYANSKIKH, V. K., KUZNETSOV, N. T., GRACHEVA, N. V., CHECHERNIKOV, V. I.,
and NUTSUBIDZE, P. V., Institute of General and Inorganic Chemistry imeni
N. S. Kurnakov, USSR Academy of Sciences

[Abstract] Gas transport methods were used in the synthesis of mixed mono-crystals of neodymium and uranium selenides which were subjected to physical chemical analysis. The results showed that Nd_2USe_5 formed rhombic crystals ($A = 7.73 \text{ \AA}$, $b = 8.41 \text{ \AA}$, $c = 12.17 \text{ \AA}$) with a paramagnetic temperature (Curie) of -240°K and an effective magnetic moment (μ_{eff}) of $54.31 \times 10^{-24} \text{ J/T}$.

$\text{Nd}_{0.5}\text{U}_{0.5}\text{Se}_2$ rhombic crystals ($a = 7.10 \text{ \AA}$, $b = 7.66 \text{ \AA}$, $c = 5.68 \text{ \AA}$) had a paramagnetic temperature of -34°K and an effective magnetic moment of $19.62 \times 10^{-24} \text{ J/T}$. Figures 3; references 3: 2 Russian, 1 Western.
[309-12172]

UDC 547.458.83:543.251.1

ELECTRODE PROPERTIES OF CATION EXCHANGE COATINGS BASED ON CELLOPHANE

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA
TEKHOLOGIYA in Russian Vol 26, No 4, Apr 83 (manuscript received 10 Apr 81)
pp 450-453

SIDERKO, V. M., MECHKOVSKIY, S. A., KAPUTSKIY, F. N. and GORBATYUK, Ye. T.,
Department of High-Molecular Compounds and Colloid Chemistry, Belorussian
State University imeni V. I. Lenin

[Abstract] Recently, wide use of carboxyl-containing materials, including ones based on cellulose, has been limited by the amount of information available on coating reaction to various ions. The authors studied selectivity of the title coatings made of cellophane processed with an alkaline solution of sodium monochloride. Then swelling, phase separation, and content of COOH and pK groups were determined. The nature of competing ions was found to be a factor in determining dissociation constants. With increased counterion radius and related decrease in hydration in the gel phase, swelling declined, but the counterion's destructive effect on absorbed water increased, bringing increased matrix solvation. The pK magnitude and charge transfer through the membrane in turn depended on solvation effects in the gel phase. A strong coion effect on membrane potential was noted, and increased concentrations of ionogenic groups brought increased negative (and reduced positive) membrane potential values. Thus complex ion-exchange processes and charge transfer to carboxyl-containing cellulose derivatives were observed. These changes can be controlled using principles of electrostatic, covalency and structural information of solvation of mobile ions in systems containing polysaccharide chains. Figures 4, references 7: 6 Russian, 1 Western.
[317-12131]

UDC: 547.26'118

MECHANISM OF INTERACTION OF PHOSPHORUS DITHIOACID AND SILYLDITHIOPHOSPHATES WITH NAPHTHOQUINONES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 5, May 83
(manuscript received 13 Jul 82) pp 1005-1009

KUTYREV, G. A., ISLAMOV, R. G., LYGIN, A. V., YAGFAROVA, L. M., CHERKASOV, R. A.,
PUDOVIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] The interaction of dithioderivatives of phosphorus with p-benzoquinone leads to S-aryldithiophosphates (III) which when heated can isomerize to O-2-mercapto-4-hydroxy-(trimethylsiloxy)-phenylthiophosphates (IV). The authors performed kinetic studies of these reactions in various solvents using deuterated reagents, showing that phosphorus dithioacids and silyldithiophosphates initially form, with p-benzoquinone, products of 1,4-attachment (II). In low basicity media the first stage defines the rate of the entire process. As nucleophilic properties of the solvents increase, the limiting stage becomes the transfer of the proton from the aromatic ring of the intermediate to the carbonyl group. This work continues the study of the comparative reactivity of phosphorus dithioacids and S-trimethylsilyldithiophosphates on the example of their reaction with 1,4- and 1,2-naphthoquinones. IR spectroscopy and differential microcalorimetry demonstrate that the interaction of dithiophosphoric acid and silyldithiophosphates with 1,4- and 1,2-naphthoquinones occur in two stages with intermediate formation of attachment products at the C=C or C=C-C=O linkage. The phosphorus dithioacid reaction mechanism depends on the structure of the initial quinone, silyldithiophosphates in all cases forming intermediate 1,4-adducts. References 8: 5 Russian, 2 Western (one by Kuttyrev, et al.).
[295-6508]

UDC: 547.118'26

REACTION OF SILYLDITHIOPHOSPHATES WITH THIONYLAMINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 5, May 83
(manuscript received 23 Jun 82) pp 1009-1013

KUTYREV, G. A., LYGIN, A. V., CHERKASOV, R. A. and PUDOVIK, A. N.,
Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] A study was made of the interaction of silyldithiophosphates with thionylamines. N-substituted thionylamines under the influence of reagents

with a mobile hydrogen atom can form either stable products of attachment at the double N-S bond or can be converted to amino derivatives. The reaction of phosphorus dithioacids with $R-N=S=O$ leads to bis-(thiophosphoryl)-disulfides, amides or amines. O, O-diisopropyl-S-trimethylsilyldithiophosphate reacts with N-phenylthionylamine to form bis-(O,O-diisopropylthiophosphoryl)-disulfide (I)-trisulfide (II), hexamethyldisiloxane and N, N-di-(trimethylsilyl)-aniline (III). The structure of the reaction products was proven by NMR and IR spectroscopy, elemental analysis and agreement of their physical constants with data from the literature. References 23: 12 Russian, 11 Western. [295-6508]

UDC: 547.241+547.37

VINYL ESTERS OF PHOSPHORUS ACIDS, PART 24: α -PHENYLVINYLPHOSPHITES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 5, May 83
(manuscript received 27 May 82) pp 1013-1021

KOLODKA, T. V. and GOLOLOBOV, Yu. G., Institute of Organic Chemistry,
Ukrainian SSR Academy of Sciences, Kiev

[Abstract] A rather general and convenient method is suggested for producing α -phenyl- β -chlorovinylphosphites, based on the interaction of trivalent phosphorus chlorides with 1-chloro- or 1,1-dichloroacetophenones in the presence of triethylamine. This leads to products of O-phosphorylation corresponding to α -phenylvinylphosphites. O-(α -phenyl- β , β -dichlorovinyl)-dichlorophosphite disproportionates when heated to form tri[O(α -phenyl- β , β -dichlorovinyl)] phosphite. O-(α -phenyl- β , β -dichlorovinyl)-pyrocatechin-N-phenyl- and O-(α -phenylvinyl)-pyrocatechin-N-phenylphosphazo compounds exist in dimer form. The constants, and results of analysis of the compounds obtained, are presented in tabular form, as are the spectroscopic characteristics. Full descriptions of the experiments which produce these compounds are presented. References 12: 8 Russian, 4 Western. [295-6508]

UDC: 547.557+547.36'118+546.183+541.127

VINYL ESTERS OF PHOSPHORUS ACIDS, PART 25: INDUCTIVE EFFECTS OF VINYLOXYL RADICALS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 5, May 83
(manuscript received 5 Jul 82) pp 1022-1028

KASUKHIN, L. F., PONOMARCHUK, M. P., KOLODKA, T. V., MALENKO, D. M., KIM, T. V. REPINA, L. A., KISELEVA, Ye. I. and GOLOLOBOV, Yu. G., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Using a kinetic method based on the Staudinger reaction, the authors estimated the inductive acceptor capacity of a number of vinyloxy

radicals with variable substituents in the α and β positions. Phosphites and amidophosphites I-XVI containing these vinyloxy groups were subjected to imination with phenylazide and the kinetic parameters of the reaction were determined azotometrically. For all of the compounds analyzed imination of the P^{III} center is limited to the first stage of formation of intermediate phosphazides which decompose rapidly, converting to imides I'-XVI'. It was found that after introduction of the first substituent to the vinyloxy group its acceptor capacity with subsequent substitution changed slightly. The inductive acceptor capacity of the compounds depends little on the nature of the substituent at the double bond. References 19: 17 Russian, 2 Western. [295-6508]

UDC: 547.341

SOME OXAPHOSPHOLENE REACTIONS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 5, May 83
(manuscript received 19 Apr 82) pp 1045-1049

NURTDINOV, S. Kh., ISMAGILOVA, N. M., FAKHRUTDINOVA, R. A. and ZYKOVA, T. V.,
Kazan Institute of Chemical Technology imeni S. M. Kirov

[Abstract] The authors previously reported that alkyl- or aryl-substituted oxaphosphol-4-enes when exposed to phosphorus pentasulfide are converted to thionoderivatives. Developing these studies, they deepened their investigation of the same reaction. It was found that with successive heating of 3,3,5-trimethyl-2-oxo-2-ethyl-1,2-oxaphosphol-4-ene with phosphorus pentasulfide in addition to thionooxaphosphol-4-ene (Ia) a product is formed in which the endocyclic oxygen atom is swapped for a sulfur atom, noted previously for 4-methyl-2,5-dioxo-2-ethyl-1,2-oxaphospholane. The cyclic derivatives of 1,2-oxaphospholenes were found to be more stable compounds. When heated for long periods of time to 120°C with phosphorus pentasulfide only the phosphoryl oxygen atom was exchanged for a sulfur atom. The structure of the products produced was confirmed by elemental analysis and spectral methods. The products of interaction of alkyl substituted thionooxaphospholenes are easily isomerized to cyclic tertiary phosphine oxides--derivatives of phosphetene; cyclic derivatives of 1,2-oxaphospholenes with three-coordination phosphorus atom are stable. Figures 2; references 5 (Russian). [295-6508]

SYNTHESIS OF NEW PHOSPHADECALONES WITH THREE- AND FOUR-COORDINATION PHOSPHORUS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 5, May 83
(manuscript received 28 Jun 82) pp 1050-1054

BOSYAKOV, Yu. G., KIM, D. G., LOGUNOV, A. P., REVENKO, G. P., SHIGANAKOVA, O.V. and RABETSKAYA, T. I., Institute of Chemical Sciences, Kazakh SSR Academy of Sciences, Alma-Ata

[Abstract] The authors synthesized 1,2-diphenyl-1-phosphabicyclo-[4,4,0]-decane-4-one using phenylphosphine and styrylcyclohexenylketone as the initial products. Reactions were performed in an atmosphere of argon with no solvents or catalysts. The yield of phosphadecalone reached 50%. In contrast to cyclization of phenylphosphine with propenylisopropenyl ketones and β,β -dimethyldivinyl ketone, which occurs exothermically, synthesis of phosphadecalone requires heating of the reaction mixture for 3 hours to 140-150°C. The bicyclic phosphorinane derivatives enter into an oxidation reaction, attaching sulfur and selenium to form stereoisomer mixtures of phosphadecalones with phosphoryl, thio- and selenophosphoryl groups. Four individual stereoisomers of oxo- and thiophosphadecalones are formed. References 12 (Russian). [295-6508]

SYNTHESIS OF PHOSPHORYLATED m-AMINOBENZOIC ACID ESTERS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 5, May 83
(manuscript received 25 Jun 82) pp 1054-1057

GPECHKIN, N. P., NIKONOROVA, L. K. and ZHELONKINA, L. A., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] Continuing studies of methods of synthesis, physical-chemical and biological properties of phosphorylated amino acids, the authors obtained certain phosphorus derivatives of meta-aminobenzoic acid by two synthesis methods. The first consists in the interaction of dialkylchlorophosphites with the corresponding meta-benzoic acid esters. The second consists in reamination of O, O-dialkylphosphorous acid amides with m-aminobenzoic acid esters. The structure of the substances produced was confirmed by IR and ^{31}P NMR spectroscopy. References 14: 12 Russian, 2 Western. [295-6508]

HYDROLYSIS OF DI-(p-NITROPHENYL)METHYLPHOSPHONATE IN PRESENCE OF POLYETHYLENE IMINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 5, May 83
(manuscript received 15 Jul 82) pp 1058-1062

BAKEYEVA, R. F., KUDRYAVTSEVA, L. A., BEL'SKIY, V. Ye. and IVANOV, B. Ye.
Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan
Branch, USSR Academy of Sciences

[Abstract] A study is made of the hydrolysis of di-(p-nitrophenyl)methylphosphonate in the presence of polyethylene imines of linear (M5000) and branched (M80,000) structure. As the concentration of polymers in water increases at constant pH there is an increase in the substrate hydrolysis rate constant, reaching its maximum value for the linear isomer. A study of the variation in catalytic activity of polyethylene imine as a function of medium pH shows an increase in rate constant with increasing pH, possibly caused by a decrease in protonization of the amino group which serves as a catalytic center and a change in the globular structure of the polyethylene imines. The catalytic activity of the polymer catalysts can be increased by increasing concentration of reagents as they are bonded by the polymer, an increase in nucleophilicity of the reagents participating in the reaction and an increase in the reactivity of the substrate in the local surrounding of the polymer microglobules. Figures 2; references 12: 7 Russian, 5 Western.
[295-6508]

SYNTHESIS OF DIETHYLPHOSPHORIC ACID ESTERS BASED ON NITROGEN CONTAINING HETEROCYCLIC COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 5, May 83
(manuscript received 27 Sep 82) pp 1181-1185

KARIMOV, D. T., DALIMOV, D. N., ABDUVAKHABOV, A. A. and GODOVIKOV, N. N.,
Institute of Bioorganic Chemistry, Uzbek SSR Academy of Sciences, Tashkent

[Abstract] To study the anticholinesterase activity, the authors synthesized esters of O,O-diethylphosphoric acids I-XIV based on nitrogen-containing heterocyclic compounds. The IR spectra confirm the structures assumed. All the compounds studied are competitive reversible acetylcholinesterase inhibitors. The variation of inhibitor activity as a function of cation head structure of the organophosphorus inhibitor is quite complex. References 6:
4 Russian, 2 Western.
[295-6508]

SEMICARBAZONES OF PHOSPHORYLATED ACETIC ALDEHYDES AND PHOSPHORYLATED KETONES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 5, May 83
(manuscript received 16 Jun 82) pp 1185-1186

LIORBER, B. G., KHAMMATOVA, Z. M., PAVLOV, V. A., SOKOLOV, M. P. and
TARZIVOLOVA, T. A., Kazan Institute of Chemical Technology imeni S. M. Kirov

[Abstract] It was found that these semicarbazones of phosphorylated acetic aldehydes can be synthesized by acting on the aldehydes with semicarbazide as a free base. Due to the slight basicity of the semicarbazide the rate of aldol condensation is lower than the formation of phosphorylated semicarbazones, allowing them to be produced with good yield. The structure of the compounds produced was confirmed by IR spectroscopy. References 2 (Russian).
[295-6508]

PHOSPHAZOREACTION IN 2-AMINO-3,5-DICYANO-4-ARYL-6-METHOXYPYRIDINE SERIES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 5, May 83
(manuscript received 12 Nov 82) pp 1187-1188

PETROVSKIY, A. S., PROMONENKO, V. K., KHASKIN, B. A., RYMAREVA, T. G. and
NAUMOVA, I. I., All-Union Scientific Research Institute of Chemical Means of
Plant Protection, Moscow

[Abstract] For the first time, 2-trichlorophosphaza-3,5-dicyano-4-aryl-6-methoxypyridines (III, IV) have been produced by the Kirsanov reaction by interacting 2-amino-3,5-dicyano-4-aryl-6-methoxypyridines (I, II) with an equimolar quantity of phosphorus pentachloride. The reaction was conducted in carbon tetrachloride with boiling or anhydrous chlorobenzene at 85 to 100°C. Compounds III and IV are white crystalline substances soluble in most organic solvents. Their structure was established by elemental analysis, IR, ³¹P NMR and mass spectra. References 2 (Western).
[295-6508]

INTERACTION OF TRIPHENYLPHOSPHINE WITH PHTHALYL IONS

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 19, No 5, May 83
(manuscript received 25 Nov 82) pp 1106-1107

OPARIN, D. A., MELENT'EVA, T. G. and PAVLOVA, L. A., Department of Metabolic Regulation, Belorussian SSR Academy of Sciences, Grodno; Leningrad Technological Institute imeni Lensovet

[Abstract] The authors showed that salts of 1,3,3-trisubstituted phthalyl ions react readily with triphenylphosphine to form previously unknown stable phthalylphosphonium salts, alkaline hydrolysis of which leads to 1-oxophthalanes. References 3: 2 Russian, 1 Western.
[299-6508]

UDC 547.241

CONFORMATION AND PROTON ACCEPTANCE BY CERTAIN DIALKYLPHOSPHITES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 4, Apr 83
(manuscript received 25 May 82) pp 774-777

BOROVIKOV, Yu. Ya. and KOVAL', N. V., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Calculated dipole moments and IR spectroscopic data for seven dialkylphosphites-- $(\text{AlkO})_2\text{HP=O}$ --demonstrated that an equilibrium prevails between forms with the alkoxy groups in the gauche-gauche' and gauche-trans orientations. Reactions of the dialkylphosphites with trichloro- and trifluoroacetic acids and with chloroform were largely limited to adduct formation. The measured enthalpies of formation were somewhat lower (-6.5 to -9.1 kcal/mole) than for dimethylsulfoxide complexes, and approximately 1.5-fold lower than the enthalpy of formation seen with trialkylphosphinoxides. References 17: 15 Russian, 2 Western.
[268-12172]

λ^3 -IMINOPHOSPHINE WITH C-P=N TRIAD: 1,3,5-TRIS(TERT-BUTYL)PHENYL-N-TRIMETHYLSILYLIMINOPHOSPHINE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 4, Apr 83
(manuscript received 16 Jun 82) pp 778-780

ROMANENKO, V. D., RUBAN, A. V. and MARKOVSKIY, L. N., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Conditions are described for the synthesis of 1,3,5-tris(tert-butyl)phenyl-N-trimethylsilyliminophosphine (I), the first reported stable iminophosphine containing the C-P=N triad. The reaction was carried out by the addition of an equimolar concentration of bis(trimethylsilyl)aminotrimethylsilyliminophosphine to lithium 1,3,5-tris(tert-butyl)phenyl in tetrahydrofuran at -78°C for 1 h, followed by 5 h of reaction at 20°C, and eventual isolation of I. The structure of I was confirmed by spectroscopic data; it represents an orange-red oily liquid that is highly susceptible to the effects of oxygen and moisture, but can be stored for days under argon. I possesses properties typical of coordinated unsaturated iminoderivatives of trivalent phosphorus, e.g., it reacts energetically with methanol in hexane to give N-trimethylsilyl-amino-O-methyl-1,3,5-tris-(tert-butyl)phenylphosphonite. References 5:

1 Russian, 4 Western.

[268-12172]

REACTION OF DIMETHYLISOCYANATOPHOSPHITE WITH α -BROMOACRYLIC ACID ESTER AND NITRILE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 4, Apr 83
(manuscript received 13 Jul 82) pp 931-932

KONOVALOVA, I. V., BURNAYEVA, L. A., TEMNIKOVA, Ye. N. and PUDOVIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] Conditions are described which demonstrated that the reaction of dimethylisocyanatophosphite (I) with α -bromoacrylic acid ester and nitrile led to the synthesis of crystalline cycloaddition products. At room temperature I reacted with methyl 2-bromoacrylate to form 4-bromo-2,2-dimethoxy-4-methoxycarbonyl-5-oxo-1,2-azaphospholene, and with α -bromoacrylonitrile to give 4-bromo-2,2-dimethoxy-5-oxo-4-cyano-1,2-azaphospholene. The structure of both products were confirmed by NMR spectroscopy. References 3 (Russian).

[268-12172]

NEW METHOD FOR PREPARATION OF ORGANOPHOSPHORUS COMPOUNDS WITH PHENACYL RADICALS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 4, Apr 83
(manuscript received 24 Jul 82) pp 935-936

FEDOROVA, G. K., ANAN'YEVA, L. G., YAKOVCHUK, O. A. and FESHCHENKO, N. G.

[Abstract] A novel method is described for the synthesis of organophosphorus compounds with phenacyl radicals which rests on the reaction of concentrated sulfuric acid with organophosphorus compounds containing β -chlorostyryl radicals. In specific terms, reaction of the acid with acid chlorides and esters of bis(β -chlorostyryl)phosphonic acid and tris-(β -chlorostyryl)phosphine oxide resulted in the synthesis of diphenacylphosphonic acid, methyl diphenacylphosphonate, ethyl diphenacylphosphonate, and tris(phenacyl)phosphine oxide. References 6: 5 Russian, 1 Western.
[268-12172]

DIALKYLPHOSPHINOTETRAMETHYLENEOXONIUM IODIDE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 4, Apr 83
(manuscript received 6 Aug 82) pp 937-938

GOMEL'YA, N. D., FESHCHENKO, N. G. and MATYUSHA, A. G., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Description is provided of the reaction of dialkyliodophosphines with tetrahydrofuran to yield dialkylphosphinotetramethyleneoxonium iodides, a new type of stable oxonium salts. The products obtained in this manner--diethylphosphinotetramethyleneoxonium iodide, dipropylphosphinotetramethyleneoxonium iodide, dibutylphosphinotetramethyleneoxonium iodide--are colorless, heat stable, crystalline substances readily soluble in water and sparingly soluble in organic solvents. These compounds are highly conductive, easily replace the iodide ion for a tosylate anion, and undergo partial decomposition on prolonged storage in air and during recrystallization. Reference 1 (Western).
[268-12172]

PHOSPHORYLATED DERIVATIVES OF 2-HYDROXYMETHYL-1,4-DIOXANE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 4, Apr 83
(manuscript received 5 Jul 82) pp 938-939

TSIVUNIN, V. S., ZARIPOVA, V. G., BIKULOVA, V. Zh. and ZYKOVA, V. V.,
Kazan Institute of Chemical Technology imeni S. M. Kirov

[Abstract] Phosphorylated derivatives of 2-hydroxymethyl-1,4-dioxane (I) were synthesized by reacting I with PCl_3 in triethylamine to form tris-2-dioxanylmethylphosphite; the latter reacted with CH_3I to give di-2-dioxanylmethylphosphonate by Arbuzov's rearrangement. Reaction of I with PCl_3 resulted in the formation of di-2-dioxanylmethylphosphorous acid, which reacted with cyclohexane to form the corresponding hydroxy derivative di-2-dioxanylmethyl α -hydroxycyclohexylphosphonate. References 3 (Russian).
[268-12172]

UDC 547.241

PHENYLBIS(TRIFLUOROMETHYL)PHOSPHINE AND OTHER PHENYLPERFLUOROALKYLPHOSPHINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 4, Apr 83
(manuscript received 11 Oct 82) pp 939-940

MASLENNIKOV, I. G., KIRICHENKO, L. N., ALEJNIKOV, S. F., LEBEDEV, V. B. and
LAVRENT'YEV, A. N., Leningrad Technological Institute imeni Lensovet

[Abstract] The synthesis of phenylbis(trifluoromethyl)phosphine (I) was achieved by dropwise addition of bis(trifluoromethyl)chlorophosphine to phenylmagnesium bromide at $-35^\circ C$ with slow mixing. The temperature was gradually raised to room level and, following overnight storage, vacuum distillation yielded I. In addition, diphenyl(trifluoromethyl)phosphine and diphenyl(pentafluoroethyl)phosphine were synthesized by methods described in the literature. ESR and NMR data are provided for these three compounds. References 6: 1 Russian, 5 Western.
[268-12172]

AMIDOPHOSPHITE PHOSPHORYLATION OF 5-HYDROXYINDOLES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 4, Apr 83
(manuscript received 14 Jul 82) pp 941-942

GUREVICH, P. A., RAZUMOV, A. I. and STEPANOV, P. A., Kazan Institute of
Chemical Technology imeni S. M. Kirov

[Abstract] Four compounds were obtained by the phosphorylation of 5-hydroxyindoles by amidophosphites by boiling for 2.5-3 h under N_2 . The reaction of equimolar concentrations of 2-methyl-3-ethoxycarbonyl-5-hydroxyindole and an amidophosphite led to the formation of 2-methyl-3-ethoxycarbonyl-5-0-phosphitoindoles; the latter reacted with sulfur during boiling for 2 h to give the respective compounds 2-methyl-3-ethoxycarbonyl-5-0,0-diethylthiophosphatoylindole, 2-methyl-3-ethoxycarbonyl-5-0,0-dipropylthiophosphatoylindole, 2-methyl-3-ethoxycarbonyl-5-0,0-diisopropylthiophosphatoylindole, and 2-methyl-3-ethoxycarbonyl-5-N,N,N',N'-tetraethyldiamidothiophosphatoylindole.

References 6 (Russian).

[268-12172]

ACYL-SUBSTITUTED VINYL ESTERS OF 1,3,2-DIOXAPHOSPHOLANES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 4, Apr 83
(manuscript received 24 Jul 82) pp 943-944

KOZENASHEVA, L. Ya., SMIRNOVA, T. V., KOLESOVA, V. A. and VIRIN, L. I.,
Moscow Institute of Chemical Technology imeni D. I. Mendeleev

[Abstract] Phosphorylation of acetoacetic ester with 2-chloro-4-methyl- and 2-chloro-4,5-dimethyl-1,3,2-dioxaphospholanes in the presence of triethylamine at 25-40°C led to the synthesis of 2-0-(1-methyl-2-ethoxycarbonylvinyl)-4-methyl-1,3,2-dioxaphospholane and 2-0-(1-methyl-2-ethoxycarbonylvinyl)-4,5-dimethyl-1,3,2-dioxaphospholane, respectively. Boiling the 4-methyl and the 4,5-dimethyl compounds with equimolar concentrations of sulfur and selenium led to the formation, respectively, of 2-0-(1-methyl-2-ethoxycarbonylvinyl)-2-thio-4-methyl-1,3,2-dioxaphospholane and 2-0-(1-methyl-2-ethoxycarbonylvinyl)-2-seleno-4,5-dimethyl-1,3,2-dioxaphospholane. The results of chemical analysis and IR spectra for these products are provided. References 4: 2 Russian, 2 Western.

[268-12172]

UDC: 577.15

INFLUENCE OF CERTAIN ORGANOPHOSPHORUS INSECTICIDES ON GRAPEVINE NITRATE
REDUCTASE ACTIVITY

Tbilisi SOOBASHCHENIYA AKADEMII NAUK GRUZINSKOY SSR in Russian Vol 109, No 2,
Feb 83 (manuscript received 29 Jan 82) pp 397-400

OGANESYAN, A. A., NUTSUBIDZE, N. N., corresponding member, Institute of Plant
Biochemistry, Georgian SSR Academy of Sciences

[Abstract] Assimilation of nitrogen is one of the major processes occurring in plants. Vegetable nitrate reductase activity is greatly stimulated in some plants by nitrogen feeding. The influence of insecticides on the assimilation of nitrogen in the grapevine remains unknown. The authors therefore studied the effect of certain organophosphorus insecticides on nitrate reductase activity in the leaves and roots of grapevines. Three-month-old grapevine seedlings grown under field conditions were placed in water one day before the experiment. They were then sprayed with a 0.2% solution of chlorophos, cyanox and gardone and immediately placed for various periods of time in a solution of 0.036 M potassium nitrate. Nitrate reductase activity was determined in the roots and leaves after 24 and 48 hours following spraying. The results indicated that gardone and cyanox stimulate the activity of the enzyme, whereas chlorophos inhibits its activity. References 12: 5 Russian, 7 Western. [285-6508]

UDC: 665.644.4

TRANSFORMATION OF HYDROCARBONS IN CATALYTIC REFORMING OF GASOLINE FRACTIONS

Moscow NEFTEKHIMIYA in Russian Vol 23, No 3, May-Jun 83
(manuscript received 5 Aug 82) pp 343-352

MASLYANSKIY, G. N., SHAPIRO, R. N., PANNIKOVA, R. F. and POTAPOVA, A. A.,
All-Union Scientific Research Institute of Petrochemical Processes

[Abstract] A study is presented of the influence of temperature, pressure and speed of transmission of raw material on the relative rates of conversion and selectivity of aromatization of hydrocarbons in catalytic reforming of gasoline fractions. The raw material was fractions boiling at 62-105°C, usually used for the production of benzene and toluene by catalytic reforming. Hydro-purification reduced the sulfur content in the raw material to $5 \cdot 10^{-5}$ mass %. Catalytic reforming was performed in a continuous flow installation with recirculation of the hydrogen-containing gas formed in the process. Industrial catalysts containing 0.36 mass % platinum were used as well as bimetallic and polymetallic commercial catalysts. It was found that decreasing pressure from 3 to 2 MPa leads to an increase in the yield of hydrogen by a factor of approximately 2; decreasing to 1 MPa--by a factor of 3. The reaction products contained no cyclohexane or methylcyclohexane, a result of the high rate of transformation of these hydrocarbons to aromatic hydrocarbons during reforming on aluminoplatinum catalysts. The data of the present work indicate that the depth of transformation of the most important raw material fractions such as hexane, heptanes and methylcyclopentane depend little on the pressure used. The rate of isomerization of hexanes and heptanes also does not vary greatly with pressure. However, changing the pressure causes a radical change in the primary direction of the transformation of the hydrocarbons, decreasing the pressure leading to a significant increase in the yield of benzene and toluene. The increased yield of toluene upon decreased pressure is related primarily to an increase in selectivity of the reaction of dehydrocyclization of heptane. Figures 4; references 15: 8 Russian, 7 Western.
[320-6508]

CONVERSION OF AROMATIC C₉ HYDROCARBONS IN PRESENCE OF HYDROGEN ON POLYFUNCTIONAL MOLYBDENUM-MORDENITE CATALYST

Moscow NEFTEKHIMIYA in Russian Vol 23, No 3, May-Jun 83
(manuscript received 4 Jun 82) pp 353-360

RABINOVICH, G. L. and CHIZHOV, V. B., All-Union Scientific Research Institute of Petrochemical Processes, Angarsknefteorgsintez Production Association

[Abstract] An attempt was made to perform selective conversion of a fraction of aromatic C₉ hydrocarbons separated from reforming gasoline with primary production of xylenes and toluene and to study the chemistry and sequence of the reactions occurring. The study was performed in the presence of polyfunctional molybdenum-mordenite catalyst. The commercial 145-175°C reforming catalysate fraction from the 105-140°C straight run gasoline fraction was used, containing 2.1% nonaromatics, 2.4% C₈ aromatics, 95.1% C₉ aromatics including isopropylbenzene, n-propylbenzene, ethyl toluenes, trimethylbenzenes, indane and 0.4% C₁₀ aromatics. The transformation of the C₉ aromatic hydrocarbon fraction with hydrogen on molybdenum-mordenite catalyst includes reactions of hydrodealkylation of benzene homologs containing 2 or more C atoms in the side chain which occurs quite rapidly with splitting of these groups, hydrodealkylation of polymethylbenzenes, disproportionation-transalkylation of methylbenzenes and isomerization of polymethylbenzenes. The balanced occurrence of these reactions at 460°C and 4.6 MPa allows conversion of low value aromatic C₉ hydrocarbon fraction to xylenes and toluenes. Figures 2; references 7: 6 Russian. 1 Western.
[320-6508]

STUDY OF COPPER-CONTAINING CATALYSTS FOR METHANOL SYNTHESIS

Moscow NEFTEKHIMIYA in Russian Vol 23, No 3, May-Jun 83
(manuscript received 13 Jul 81) pp 394-398

KOSTROV, V. V., MOROZOV, L. N. and NOVIKOV, Ye. N., Ivanovo Institute of Chemical Technology

[Abstract] Model specimens were prepared by saturating formed γ -Al₂O₃ with aqueous solution of salts of copper and zinc with subsequent heat treatment. The catalytic properties were determined on continuous flow circulation installations at atmospheric pressure in a gas mixture consisting of 27% CO, 55% H₂, 18% N₂, 300-1000 mg H₂O/m³. The reaction products were frozen in a liquid nitrogen trap, then chromatographically analyzed. The results of the experiment established that a CuO/ γ -Al₂O₃ system catalyzes the synthesis of methanol. As the copper content increases to 13-14 mass %, the activity of the

catalyst increases. The activity and selectivity for synthesis of methanol depend on the status of the copper on the surface of the $\gamma\text{-Al}_2\text{O}_3$, the relationship between copper and zinc components and the intensity of hydroxyl coverage of the surface. The formation of side products results largely from the capability of the catalytic system to generate active hydrogen, and the degree of oxidation of the copper component under the process conditions. Figures 3; references 8: 5 Russian, 3 Western.
[320-6508]

UDC: 665.6.033.52:543.422

STRUCTURE-GROUP COMPOSITION OF ORGANIC SULFUR COMPOUNDS OF GAS CONDENSATE FROM URTABULAK DEPOSIT, UZBEK SSR

Moscow NEFTEKHIMIYA in Russian Vol 23, No 3, May-Jun 83
(manuscript received 28 Apr 82) pp 424-428

AGADZHANOVA, N. V., LYAPINA, N. K., ALIYEVA, R. B., SHMAKOV, V. S. and PARFENOVA, M. A., All-Union Scientific Research and Planning Institute for Preparation for Transportation and Processing of Natural Gas, Baku; Institute of Chemistry, Bashkin Branch, USSR Academy of Sciences, Ufa

[Abstract] A study is presented of the structure-group composition of organic compounds of sulfur from the gas condensate of the promising Urtabulak deposit of Central Asia. It is similar to the condensates of the Dengizkul' and Khauzak deposits, which are not presently exploited. The organic sulfur compounds from the gas condensate were extracted with 87 and 91% sulfuric acid. It was found that the sulfide portion of the organic sulfur compounds consists primarily of thiamino-, thiabicycloalkanes and dialkylsulfides. The thiophene portion is represented by alkyl-substituted thiophenes and benzothiophenes. References 13 (Russian).
[320-6508]

UDC: 541.15+577.391:615.45

RADIATION STERILIZATION PROBLEMS

Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 17, No 3, May-Jun 83
(manuscript received 28 Dec 82) pp 233-243

TAL'ROZE, V. L. and TROFIMOV, V. I., Institute of Chemical Physics, USSR Academy of Sciences; Scientific Research Institute of Biological Testing of Chemical Compounds

[Abstract] There are no sterilization methods which can assure complete death of 100% of all microflora without damaging the object being sterilized, though the probability of residual microbial populations can frequently be made extremely small. The capability of microorganisms for reproduction depends on their cultivation conditions, so that a cell considered dead in that it does not multiply in an artificial medium may develop in a living organism. Finally, there is no method available today for testing the achievement of full sterility. For this reason, the concept of sterility is being replaced with that of "microbiologic safety," which can be numerically described by the degree of reliability. All sterilization methods are divided into two groups: removal of microorganisms from the object and suppression of their capability for reproduction. Methods of sterilization based on destruction of microorganisms are more widely used today. However, sterilization by heat is unsuitable for substances such as medications which are not heat tolerant. Radiation sterilization is being increasingly used, particularly in such situations. The situation of radiation sterilization in terms of its effectiveness and its effects on the objects being sterilized is quite briefly described. It has a number of definite technological advantages over other sterilization methods, including the possibility of sterilizing products in sealed packages so that sterility can be maintained until the moment of use, controllability of effectiveness, which varies almost directly with absorbed dose and low cost. The assurance of safety of the products sterilized in terms of their residual radioactivity is a more difficult problem. The authors have studied the influence of the composition of an injection solution and conditions of its freezing on the local concentration of an organic additive in solution following radiation sterilization. It was established that at realistically achievable freezing rates the average local concentrations of organic substances in ice depend on the salt composition of the aqueous solution frozen, and in systems with uniform distribution of the additive radiation decomposition is greater than in media in which the local concentration is 2 to 3 orders of magnitude greater than in the liquid phase. Injection preparations of insulin can be produced in the form of solutions or suspensions. Many

experiments with model systems and actual aqueous injection solutions have shown that when aqueous solutions of drugs are frozen the indirect effects of radiation are prevented and the preparations are stabilized to radiation effects, preventing decomposition of the active substances in the injection solutions. The problem has in principle therefore been solved and the question for today is one of practical utilization of radiation sterilization of medications. Figures 6; references 36: 13 Russian, 23 Western.
[310-6508]

UDC 340.67:615.9:615.285.7

COMPARATIVE EVALUATION OF METHODS FOR ISOLATING CIDIAL FROM CADAVER MATERIAL

Moscow FARMATSIYA in Russian Vol 32, No 3, May-Jun 83
(manuscript received 30 Jun 81) pp 28-30

IKRAMOV, L. T. and SAIDVALIYEV, A. K., Tashkent Pharmaceutical Institute

[Abstract] Since the effects of the organophosphorus pesticide cidial has received little attention from the point of view of forensic chemistry, the authors attempted to isolate the substance from cadaver liver material by steam distillation followed by chloroform extraction or with acid-alcohol or acidified water from both acid and alkaline solutions. These methods were not successful (from biological materials), so a steeping method using various organic solvents was tested. The best variant involved five repetitions of the steeping process with ether, with pH of 5.0-6.0. References 7 (Russian).
[298-12131]

UDC 615.246.9:661.183.2].015.2:615.382].032.018.5].036.8

ADSORPTION PROPERTIES OF ACTIVATED CHARCOAL WHEN COVERED BY PLASMA

Moscow FARMATSIYA in Russian Vol 32, No 3, May-Jun 83
(manuscript received 25 May 82) pp 40-43

LUZHNIKOV, Ye. A., GOL'DIN, M. M. and STRAKHOVA, N. M., Scientific Research Institute for Emergency Aid [Skoraya Pomoshch] imeni N. V. Sklifosovskiy, Moscow

[Abstract] Wide use of activated charcoal to remove poison from the body has led to hemomorphological changes related to reaction between blood components and the carbon. Plasma (more precisely, the proteins in plasma), collodion, albumin and other substances have been tried as coatings to prevent this reaction. The authors studied the adsorption of barbital on SKT-6A charcoal that had been processed with a coating solution containing 2.0, 0.4 and 0.04 ml of plasma per gram of sorbent. Subsequent tests with US and German equipment indicated that these plasma concentrations brought reduced adsorption of barbital by roughly 35%. An albumin variant to the test had little effect in

reducing adsorbence, indicating that a plasma-protein concentration of less than 0.04 ml/g could be used for hemosorption. Timed tests indicated that 5 minutes was sufficient for barbital adsorption. Figure 1, references 12: 8 Russian, 4 Western.
[298-12131]

UDC 615.014.42.074

EVALUATION OF THERMAL STABILITY OF DRUGS

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 17, No 5, May 83
(manuscript received 2 Jun 82) pp 623-625

POPKOV, V. A., First Moscow Medical Institute imeni I. M. Sechenov

[Abstract] Thermal destruction of drugs is accompanied by absorption or emission of heat and gaseous products. As a rule, the most informative methods for evaluation of thermal stability are thermography and thermogravimetry. Two examples have been reported: differential curves of heating some derivatives of nitrofurane and a derivatogram of ethoxide, correlating endothermal effects on the differential heating curve with the behavior of these compounds during melting process. Figures 2; references: 23 (Russian).
[297-7813]

UDC: 541.15

RADIATION ION POLYMERIZATION AT LOW TEMPERATURES: ETHYLENE OXIDE IN VITREOUS BUTYL CHLORIDE MATRIX

Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 17, No 3, May-Jun 83
(manuscript received 19 Aug 82) pp 249-252

KICHIGINA, G. A., MUYDINOV, M. R., KIRYUKHIN, D. P. and BARKALOV, I. M.
Institute of Chemical Physics, USSR Academy of Sciences

[Abstract] Results are presented from a study of low temperature post-polymerization of ethylene oxide with softening of its butyl chloride matrix. Study of the phase state of the specimens and ethylene oxide polymerization kinetics was performed using a calorimetric method. The rate of polymerization and integral polymer yield were calculated from calorimetric measurement data using the specific heat of polymerization measured in separate experiments. The polymer yield was determined also by a gravimetric method after removal of the unreacted monomer at room temperature and evacuation to a constant weight. The results indicate a cation mechanism of polymerization of ethylene oxide under the experimental conditions. Figures 4; references 7 (Russian).
[310-6508]

UDC: 533.924;541.1

SOME RESULTS OF EXPERIMENTAL STUDY OF INTERACTION OF LOW TEMPERATURE PLASMA WITH POLYMER SURFACES

Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 17, No 3, May-Jun 83
(manuscript received 18 Mar 82) pp 253-257

IVANOV, S. I., Sofia University, Bulgaria

[Abstract] Results are presented from a study of chemically pure film specimens of polyethyleneterephthalate, polyacrylonitrile, polyethylene, polyamide and cellulose subjected to plasma chemical treatment. Changes in contact wetting angle of the polymer surfaces with water due to the barrier discharge effect were studied, as well as chemical changes occurring upon exposure to a high frequency low pressure discharge. The polymer specimens which were activated were placed in a closed tubular reactor through which the working gas was passed at $5 \text{ cm}^3/\text{s}$. The reactor consisted of two cylindrical coaxial electrodes of stainless steel, between which was a dielectric barrier consisting of a

quartz tube, plus the polymer specimens. A sine wave voltage at 50 Hz, 8 kV amplitude, was applied between the electrodes, causing ignition and combustion of a quiet barrier discharge in the interelectrode area of the reactor with a discharge current density of $10 \mu\text{A}/\text{cm}^2$. In some cases a pulse discharge was produced by a thyristor generator with a repetition frequency of 450 Hz and a maximum amplitude of 40 kV. It was found that under the conditions selected the mechanism of interaction of the gas discharge plasma with the polymers was ionic. The polymer relaxation time was on the order of 10^3 hr following discharge activation. This corresponded to the life-time of the electric charges induced in the polymer during the interaction. The degree of activation was independent of the plasma forming gas, the time required to reach saturation decreasing with an increase in discharge intensity. The change in contact wetting angle is therefore assumed to be related to the electrostatic component of adhesion. Ion bombardment caused destruction of the polymer in all specimens used with all plasma forming gases tested. The high energy of the ions caused decomposition of the polymers to elements, not monomers. Figures 4; references 8: 3 Russian, 1 Czech, 4 Western.
[310-6508]

UDC: 648.745

INFLUENCE OF CONCENTRATION OF CERIUM (IV) IONS ON ISOTHERMIC POLYMERIZATION OF ACRYLONITRILE IN PRESENCE OF BROMIDE IONS

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 26, No 5, May 83 (manuscript received 29 May 81) pp 606-608

KARPENKO, G. B., AGEYEV, A. I. and ROSKIN, Ye. S., Leningrad Institute of Textile and Light Industry imeni S. M. Kirov, Department of Physics, Colloid and Analytic Chemistry

[Abstract] A study was made of the influence of concentration of cerium (IV) ions on acrylonitrile polymerization under isothermal conditions at 20 to 50°C with and without bromide ions present. Experiments were performed by the method described in the previous work of the authors except that the polymerization time remained constant at one hour, the concentration of cerium (IV) ions introduced to the reaction mixture in the form of a 0.1 M solution of cerium ammonium nitrate in 1 M nitric acid was varied. The medium used was either water or a solution of potassium bromide of assigned concentration. The pH of the reaction mixture was held at about 1, in experiments with low concentration of cerium (IV) ions it was held at this limit by the addition of the required quantity of 1 M nitric acid. The yield of the polymer increased with increasing cerium (IV) ion concentration. The suggested $\text{Ce}^{4+}\text{-Br}^-$ initiation system allows broad variation of the induction period, yield and molecular mass of the polyacrylonitrile produced. The following conditions were found to be optimal: temperature 30°C , concentration of cerium (IV) ions 0.06% ($4.5 \cdot 10^{-3} \text{ mol/l}$), concentration of bromide ions 0.01-0.02 g-ion/l. Figures 4; references 3 (Russian).
[308-6508]

INFLUENCE OF REPLACEMENT OF HYDROGEN WITH DEUTERIUM AND RELATED MONOMER VARIATIONS ON THERMODYNAMIC PROPERTIES OF POLYSTYRENE AT 0-350K

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 270, No 1, May 83
(manuscript received 17 Nov 82) pp 129-132

LEBEDEV, B. V., SMIRINOVA, N. N., LEBEDEV, N. K., KOZYREVA, N. M., KIRILIN, A.I. and KORSHAK, V. V., academician, Scientific Research Institute of Chemistry, Gorkiy State University imeni N. I. Lobachevskiy; Moscow Institute of Chemical Technology imeni D. I. Mendeleev

[Abstract] Results are presented from calorimetric studies of the influence of replacement of hydrogen with deuterium on the thermodynamic properties and enthalpy of styrene polymerization. Isobaric heat capacity c_p^0 of polystyrene, a number of its deuterium derivatives and a copolymer of styrene with deuterostyrene (molar ratio components 1:1) were measured in an adiabatic vacuum calorimeter in the 7-330K interval with an accuracy of about 0.2%. The polymers were obtained by polymerization of the corresponding monomers by the usual methods. All polymers were high molecular weight products. Viscosities in toluene are presented, as are the mean molecular masses. The thermodynamic functions were calculated for all of the polymers produced. The thermal effects of styrene polymerization and deuterostyrene polymerization in mass at 350K were measured in the presence of 0.2% benzoyl peroxide to determine the isotopic effect on polymerization enthalpy. The isotopic effect is not great, not over the error of measurement of polymerization enthalpy. Figures 3; references 8 (Russian).
[283-6508]

UDC 541.64:546.3

OBTAINING METAL-CONTAINING POLYMERS IN DONOR SOLVENTS

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 26, No 4, Apr 83 (manuscript received 1 Jun 81)
pp 486-490

GREKOV, A. P., OTROSHKO, G. V., ZBANATSKAYA, N. L. and TKACH, V. P., Department of Chemistry, Kiev Pedagogical Institute; Institute of Chemistry of High-Molecular Compounds, UkSSR Academy of Sciences

[Abstract] Earlier studies (SINTEZ I FIZIKOKHIMIYA POLIMEROV, issue 22, 1978, pp 28-31) showed that compositional materials containing metals can be obtained by treating polyurethanosulfoheptacarbazides with metal salts, resulting in improved durability, thermal and light resistance and resistance to acids and alkalis. The authors studied additional versions of this reaction using copper acetate in donor solutions at various temperatures. Results showed that in all studied solvents and in series of solvents with small polymer

concentrations, the Lambert-Beer law was valid. Maximum absorption came at 700 nm, and showed no noticeable shift in the transition from one solvent to another. With increased polymer concentrations, the absorption band intensity declined, indicating reaction of the copper ions with the polymer ligand. The highest association constant was in hexamethylphosphoramide, and the lowest in dimethylformamide. The linear dependency $\Delta H - \Delta S$ was a general pattern for donor-acceptor reaction. Use of solvents with high donor numbers resulted in increased durability for the complexes formed. Figures 5, references 11 (Russian).

[317-12131]

UDC: 541.127:547.785.5

KINETICS OF SYNTHESIS OF CERTAIN 2-ALKYLBENZIMIDAZOLES

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 49, No 6, Jun 83
(manuscript received 27 Oct 82) pp 643-647

KOROLEVA, V. R., NIKULINA, L. Ye. and CHERNENKO, V. G., Chernigov Branch,
Kiev Polytechnical Institute

[Abstract] A study was made of the process of curing of epoxy resins in the presence of 2-alkylbenzimidazoles (ABI). The kinetics of synthesis of 2-methylbenzimidazole (MBI), 2-ethylbenzimidazole (EBI) and 2-propylbenzimidazole (PBI) from o-phenylenediamine (o-PDA) and acetic, propionic and butyric acids was studied in the presence of o-phosphoric acid as a catalyst by computer modeling methods in order to determine a simple method of synthesizing ABI so that it might be used as an epoxy curing accelerator. The studies were performed at o-PDA concentrations of 2.4-2.5 mol/l and o-PDA:acid ratios of 1:1 and 1:2. The experimental reactions were performed in a 3-necked flask with a stirrer and reflux cooler but without distillation of the reaction water in a CO_2 atmosphere. The reactions of synthesis of MBI, EBI and PBI were studied at 70, 80, 90, 100, 110 and 120°C with both o-PDA:acid ratios. Estimates of dispersions of deviation obtained by modeling are presented in tabular form. Figures 3; references 6: 5 Russian, 1 Western.

[322-6508]

MODIFICATION OF LOW PRESSURE POLYETHYLENE IN PRESENCE OF 9,10-PHENANTHRENE-QUINONE

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 49, No 6, Jun 83
(manuscript received 10 May 82) pp 653-656

PATSULA, O. V., MYSHKO, V. I., KACHAN, A. A. and YAKOVLEV, V. B.,
Department of Petrochemistry, Institute of Physical-Organic Chemistry and Coal
Chemistry, Ukrainian SSR Academy of Sciences

[Abstract] Preliminary studies of the cross linking of various types of low pressure polyethylene in the presence of sensitizers such as chloroanthraquinone, anthraquinone, benzoquinone and phenanthrenequinone (PQ) have established that phenanthrenequinone is a very effective sensitizer of photochemical cross linking of low pressure polyethylene. The present report deals with a study of certain specifics of the process of cross linking of low pressure polyethylene in the presence of PQ. The compound studied were two types of low pressure polyethylene: PE-20906-040 and PE produced in the presence of a vanadium catalyst (VPE) with melt index 3.2. The ash content was 0.05 and 0.29 mass % for the two types of polyethylene. Specimens were prepared by hot pressing. The content of PQ in both specimens was 0.2 mass %. The melting point of the PQ was 210°C. Specimens were irradiated by a tungsten lamp with light filters cutting off the area of wavelength over 410 nm, thermal radiation being absorbed by a water filter. The individual processes of conversion of PQ occurring in the polymer were performed in hexane or ethanol deaerated by freezing in a vacuum. UV absorption spectra were obtained, as were luminescence spectra. Mechanical characteristics were determined on a tensile testing machine. When PQ was used as a sensitizer for photochemical cross linking of low pressure polyethylene the process occurred in several stages, the photochemical and thermal as well as structural conversions occurring during hot pressing being all important. Pressing decreased the crystallinity, helping to increase the process of cross linking upon irradiation. A portion of the PQ was also reduced to its semiquinone or corresponding hydroquinone by dehydrogenation of low pressure polyethylene and formation of PQ complex with variable valence metals, rather stable in air. Cross linking of low pressure polyethylene resulted from the interaction of macroradicals formed upon reduction of the sensitizer and decomposition of the semiquinone complex. The hydroquinone did not participate in the process of polyethylene cross linking by visible light. Figures 4; references 12: 7 Russian, 5 Western.

[322-6508]

UDC: 621.378.33

CHEMICAL PROCESSES IN $\text{CO}+\text{N}_2+\text{He}^3$ GAS PLASMA IN ACTIVE ZONE OF NUCLEAR REACTOR

Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 17, No 3, May-Jun 83
(manuscript received 20 May 82) pp 266-269

BATYRBEKOV, G. A., KOSTRITSA, S. A. and KHAZENOV, M. U., Institute of Nuclear Physics, Kazakh SSR Academy of Sciences

[Abstract] Chemical processes were modeled in a $\text{CO}+\text{N}_2+\text{He}^3$ mixture in the field of radiation of a steady nuclear reactor with a thermal neutron flux density of up to $10^{14} \text{ cm}^{-2} \text{ s}^{-1}$. Differential equations were solved, tracing the evolution of positive and negative ion densities with time and, also, the concentration of impurities. Analysis of literature data on reaction rate constants shows that the accuracy of the calculated curves is 30 to 50%. Processes requiring determination of the electron distribution function by energies are calculated with less accuracy. The method of calculation leads to good agreement, around 15%, with experimental data on radiolysis of CO for the most important processes such as the formation of CO_2 . Figure 1; references 9 (Russian).
[310-6508]

UDC 546.791+547.828

REACTION OF ANHYDROUS UO_2Cl_2 WITH TRIETHYLAMINE IN ACETONE

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 28, No 6, Jun 83
(manuscript received 24 Apr 82) pp 1531-1537

KOBETS, L. V., KOPASHOVA, I. M. and BEND', N. G.

[Abstract] Studies were conducted on formation of a complex in acetone in the reaction of anhydrous UO_2Cl_2 with triethylamine in ratios ranging from 1:0.5 to 1:10 for the respective reagents. A number of complexes were formed to which were assigned the following formulas based on extensive physicochemical analyses: $(\text{C}_2\text{H}_5)_3\text{NH}[\text{U}_2\text{O}_5\text{Cl}_3(\text{CH}_3)_2\text{CO}(\text{C}_2\text{H}_5)_3\text{N}]$, $(\text{C}_2\text{H}_5)_3\text{NH}[\text{U}_2\text{O}_5\text{Cl}_3(\text{C}_2\text{H}_5)_3\text{N}]$, and $\text{C}_2\text{H}_5\text{NH}[\text{U}_3\text{O}_8\text{Cl}_3(\text{CH}_3)_2\text{CO}(\text{C}_2\text{H}_5)_3\text{N}]$. The type of complex formed depended on both the ratio of the reagents and the concentration of UO_2Cl_2 . The reaction

involved ionization of the starting substrates, formation of chlorine ions and protonation of the amine fragments, as well as polymerization of the uranyl groups into -U-O-U bridges. Figures 2; references 12: 6 Russian, 6 Western. [309-12172]

UDC 548.736

NEUTRONOGRAPHIC STUDIES ON $\text{UO}_2\text{H}(\text{PO}_3)_3$ MONOCRYSTALS

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 28, No 6, Jun 83
(manuscript received 26 Apr 82) pp 1538-1541

SARIN, V. A., LINDE, S. A., FYKIN, L. Ye., DUDAREV, V. Ya. and GORBUNOVA, Yu.Ye.
Institute of General and Inorganic Chemistry imeni N. S. Kurnakov, USSR
Academy of Sciences

[Abstract] Neutronographic studies were conducted on $\text{UO}_2\text{H}(\text{PO}_3)_3$ monoclinic crystals to confirm structural findings obtained with x-ray diffraction and to determine the coordinates of the hydrogen atoms. The findings on the hydrogen atom coordinates and anisotropic thermal parameters are presented in a tabular form; furthermore, the distance between oxygen atoms of the phosphate group and UO_2^{2+} was 2.37 Å on the average. U-O distances in U-O fragments in which the oxygen atoms did not participate in hydrogen bonds were calculated at 1.75 Å, and in those fragments in which oxygen atoms served as proton acceptors in hydrogen bonds the U-O distance was 1.78 Å. In the polyphosphate chains the mean P-O bond-length range was 1.471 to 1.582 Å. The O-H distances and P-O-H angles were in agreement with those commonly reported in the literature, while the P-O-P bond angles ranged from 130.1 to 142.4 Å. O-O distances in O-H...O hydrogen bonds were at the lower end of the range (2.60 Å) and suggestive of the major contribution of the ionic component to the bond energy. Figures 1; references 4: 2 Russian, 2 Western. [309-12172]

INTERACTION KINETICS OF URANIUM OXIDES WITH LIQUID NITROGEN TETROXIDE

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 28, No 6, Jun 83
(manuscript received 26 Apr 82) pp 1542-1546

KLAVSUT', G. N. and KOBETS, L. V., Scientific Research Institute of Applied Physical Problems imeni A. N. Sevchenko, Minsk

[Abstract] Studies were conducted on the kinetics and activation energies of the reaction of various uranium oxides with nitrogen tetroxide in sealed ampules at temperature ranging from 20 to 150°C. Evaluation of the kinetic plots ($\lg K$ vs. $1/T$) demonstrated that the reactions were diffusion-controlled and that the calculated energies of activation for reactions involving ϵ - UO_3 , U_3O_8 , and UO_2 were, respectively, 12740, 13610 and 18090 cal/mole. At all temperatures the product formed was nitrosonium trinitratouranylate ($NO[UO_2(NO_3)_3]$; NTN). On the basis of the activation energies it appears that the reaction of UO_2 and U_3O_8 with N_2O_4 requires the initial oxidation of uranium to the +6 state, with subsequent transformation of the oxide into NTN. Figures 3; references 13: 1 Polish, 8 Russian, 4 Western.
[309-12172]

UDC: 678.763.01.028.046

INFLUENCE OF SMALL QUANTITIES OF ORGANOSILICON COMPOUNDS ON RHEOLOGIC PROPERTIES OF CARBON CHAIN RUBBER MIXTURES AND TECHNICAL PROPERTIES OF RUBBERS

Tbilisi SOOBASHCHENIYA AKADEMII NAUK GRUZINSKOY SSR in Russian Vol 109, No 1, Jan 83 (manuscript received 25 Sep 81) pp 81-84

BUKANOV, A. M., TIMOFEYEV, S. Ye., OTOPKOVA, M. A., KHANANASHVILI, L. M., corresponding member, Georgian SSR Academy of Sciences, and KORNEV, A. Ye., Tbilisi State University

[Abstract] A study was made of the influence of various oligoorganosiloxanes in model rubber mixtures based on DSSK-18 with zinc oxide 3 parts by weight, stearic acid 2 parts by wt., PM-100 50 parts by wt., diaphen FP 1.5 parts by wt., antilux 1.5 parts by wt., sulfenamide C 1 part by wt., and sulfur 2 parts by wt. It was found that when polymethylsiloxane liquid and oligoorganosiloxane with functional alkoxyl and hydroxyl groups were added, the work expended in mixing monotonically decreased with an increase in the quantity of additive due to a decrease in viscosity of the system and, consequently, facilitation of workability of the rubber mixtures. The addition of these additives increases crack growth resistance by up to 112%. The modifying influence of oligoorganosiloxanes was thus shown to improve the technological properties of rubber mixtures when introduced in small quantities (1 to 3 mass parts), decreasing power consumption, shrinkage during spraying, and increasing profiling speed. Figures 6; references 4 (Russian).
[284-6508]

STUDY OF INFLUENCE OF QUATERNARY AMMONIUM SALTS ON PROPERTIES OF SKI-3 COMPOSITIONS

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNLOGIYA in Russian Vol 26, No 5, May 83 (manuscript received 29 May 81) pp 609-612

OVCHAROV, V. I., BURMISTR, M. V., BLOKH, G. A. and SVETKIN, Yu. V.,
Dnepropetrovsk Institute of Chemical Technology imeni F. E. Dzerzhinskiy,
Department of Rubber Technology

[Abstract] A study was made of the influence of quaternary ammonium salts on the combination of properties of rubber mixtures and vulcanizates based on the nonpolar raw rubber SKI-3. The unfilled rubber mixtures used have the following composition, parts by weight: SKI-3 - 100.0; altax 0.6; diphenylguanidine 3.0; sulfur 1.0; zinc oxide 5.0; stearic acid 1.0; quaternary ammonium salts (C_2H_5)₄NBr 0.25-5.0. The introduction of tetraethylammonium bromide (TEA-Br) decreases the viscosity of the compositions, increasing the resistance of the mixture to early vulcanization and decreases the vulcanization speed. The results of testing of the rubbers at the vulcanization optimum, which was the same for all samples, showed that the main physical and mechanical properties of the rubbers with quaternary ammonium salts at 0.25-1.0 parts by wt. were equivalent to the control specimens. Data on the electrical properties of filled vulcanizates indicate that the introduction of small quantities of surfactants (0.25-0.75 parts by weights) neutralizes the surface charge of the filler. Further increases in cation-active surfactant increase the conductivity of the composition due to the excess charges. Figures 3; references 6 (Russian).
[308-6508]

UDC: 539.3:678.43

STUDY OF VARIATION BETWEEN RELAXATION AND DEFORMATION PROPERTIES OF FILLED RUBBERS

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNLOGIYA in Russian Vol 26, No 5, May 83 (manuscript received 5 Jun 81) pp 613-616

CHERNYKH, Z. V., YERMOLAYEV, V. A., ZAKHAROV, N. D. and OVCHINNIKOVA, V. N.
Yaroslavl Polytechnical Institute, Department of Chemistry and Technology of Elastomer Processing

[Abstract] The purpose of this article was to study the specifics of relaxation properties of filled rubbers by determining the relaxation time spectra and elastic hysteresis properties upon secondary deformation, and to study the interactions among them. The studies were performed on filled rubbers based on SKS-30, SKMS-30ARK and KR-50 nairit raw rubbers. The fillers used were

technical charcoal types DG-100 and PM-100 at 50 mass parts. Vulcanizates with various types of cross-links were tested, provided by the systems sulfur-plus-altax, sulfur-plus-DFG and thiuram. The number of cross-links for SKS-30 vulcanizates was $7 \cdot 10^{19}$ and $8.5 \cdot 10^{19} \text{ cm}^{-3}$. The work experimentally established the variation between relaxation and certain deformation properties of filled rubbers expressed as satisfactory correlation between the height of the relaxation time spectrum and quantities characterizing the elastic-hysteresis properties and fraction of operating cross section. This variation was observed for all systems studied. The data produced can be used to predict that with insufficiently developed framework there should be a negative influence on the operating qualities of systems of elevated intermolecular interaction such as rubber-filler, filler-filler, which agrees, for example, with the increase in fatigue endurance of rubbers made of crystallizing raw rubber during testing in repeated extension under conditions with a static component with constantly acting framework deformation. References 10 (Russian).
[308-6508]

UDC: 541.15

RADIATION CHEMICAL TRANSFORMATIONS IN AQUEOUS NAPHTHALENE SOLUTIONS

Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 17, No 3, May-Jun 83
(manuscript received 18 Feb 82) pp 244-248

BORTUN, L. N., VYSOTSKAYA, N. A. and REKASHEVA, A. F., Institute of Physical Chemistry imeni L. V. Pisarzhevskiy, Ukrainian SSR Academy of Sciences

[Abstract] Results are presented from studies of the influence of gamma radiation on aqueous solutions of naphthalene, representing a simple condensed system which can be used as a convenient model to study the mechanism of action and kinetics of radiation-chemical transformation of multinuclear aromatic hydrocarbons. The initial naphthalene was purified by repeated sublimation until its melting point agreed with reference handbook data. The naphthalene charge was then dissolved in acetone and placed in a one liter flask, then the acetone was evaporated by passing through a current of air at 20 to 25°C, after which 500 ml of double distilled water was added to the flask. The flask was intensively shaken for at least 3 hours to achieve maximum dissolution, then the undissolved naphthalene was filtered off. The naphthalene concentration before and after irradiation, as well as the concentration of mononaphthols in the solution after irradiation were determined by gas chromatography of 100 ml samples and three times chloroform extraction of 15 ml samples. The combined extract was concentrated and analyzed on a Varian chromatograph on a column filled with 80% PEHA on N-Syper chromatone, column length 1.5 m, diameter 3 mm. It was found that by irradiation of naphthalene solutions with doses of up to 0.5 kGr, dose rate 0.12, 0.54, and 1.4 Gr/s that radiation chemical consumption of each naphthalene molecule per 100 eV absorption of energy is independent of dose rate. GLC of the radiolysis products discovered 1- and 2-naphthols, primarily the former. Up to 0.20-0.25 kGr of the naphthalene consumption follows a first order kinetic equation. The results of the work thus demonstrated that the characteristics of radiolysis of aqueous solutions of naphthalene result from its high reactivity not only for OH radicals, but also for H atoms and e_{aq}^- and the competition of radical products of radiolysis of water in the reaction with the substrate. Figures 4; references 6: 4 Russian, 2 Western.

[310-6508]

USE OF SEMIPERMEABLE MEMBRANES TO PURIFY AQUEOUS SOLUTIONS OF CHLORINE, CALCIUM AND MAGNESIUM IONS

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNLOGIYA in Russian Vol 26, No 5, May 83 (manuscript received 24 Dec 82) pp 636-637

BRAGER, N. N., MOROZ, V. V. and BLAZHKO, L. G., Dneprodzerzhinsk Industrial Institute imeni M. I. Arsenichev, Department of Chemical Production of Process Technology and Automation

[Abstract] Increasing attention has recently been given to reverse osmosis as a new method of desalination of water. However, information in the literature in most cases is quite insufficient to allow estimation and selection of various semipermeable membranes for the solution of practical problems. The purpose of this work was therefore the study of a number of semipermeable membranes produced in the Soviet Union for the process of purification of aqueous solutions to remove the ions of chlorine, calcium and magnesium by reverse osmosis. The objects studied were acetate-cellulose membranes type MGA-80, MHA-90, MGA-95, MGA-100 and oxyethylene cellulose membrane type OEM-80. The studies used a specially prepared model chloride solution containing chlorides of sodium, calcium and magnesium at a total concentration of 9207 mg/l, including 3527 mg/l sodium ions, 65 mg/l calcium ions, 15 mg/l magnesium ions and 5600 mg/l chloride ions. The influence of pressure on the permeability of various membranes is shown in tabular form. The experiments established that acidification of the model solution at 6 to 10 MPa, to pH 5.6-5.7 increases selectivity: MGA-100 membrane is 92-97% selective for chlorine ions, MGA-90 and MGA-95 membranes are 97-98% selective for calcium ions, MGA-90 is 91% selective for magnesium ions. Acidification of the solution had no positive influence on the remaining ion-membrane combinations. Experiments with waste water formed in the production of chlorine and caustic by the diaphragm method were performed to gain additional information. The results of these experiments confirmed the high selectivity of membranes MGA-90 and MGA-95 for the purification of waste waters, removing ions of chlorine, calcium and magnesium. Figures 2; references 5 (Russian).
[308-6508]

UDC: 547.458.81:546.174

INFLUENCE OF NITROGEN TETROXIDE ON CELLULOSE STRUCTURE AND PROPERTIES, PART 1:
FORMATION OF COMPLEX CELLULOSE COMPOUNDS WITH NITROGEN TETROXIDE

Riga KHIMIYA DREVESINY in Russian No 3, May-Jun 83
(manuscript received 3 Aug 82) pp 13-18

GERT, Ye. V., SOKARRAS MORALES, A., MAKARENKO, M. V. and KAPUTSKIY, F. N.,
Scientific Research Institute of Physical Chemical Problems, Belorussian
State University imeni V. I. Lenin

[Abstract] Specimens of cellulose I (long fiber cotton, cotton and wood cellulose) and cellulose II (mercerized cellulose and hydrate cellulose fiber) were treated with nitrogen tetroxide N_2O_4 . Radiographs of the fibers were made with a continuous scanning scintillation counter. X-ray diagrams of air-dried specimens of various types swollen in N_2O_4 differed from the diagrams of the initial specimens, but did not reveal an amorphous swollen state. There was some similarity of the diffraction curves of cellulose- N_2O_4 complexes with the diffraction curves of cellulose- HNO_3 complexes, a result of intracrystalline swelling of the cellulose in 66% HNO_3 . Two main types of structure formed under different processing conditions were found. The interaction of cellulose with N_2O_4 does not result in the breakdown of the crystalline areas of the polymer structure as was earlier supposed. The swelling compounds which develop are clearly seen radiographically on the basis of appearance of interferences indicating crystalline structure of the complexes formed with a new elementary cell. The change in parameters of the crystalline cell of the initial material results from introduction of molecules of swelling agents into the crystalline lattice of the cellulose. Figures 4; references 15: 13 Russian, 2 Western.
[300-6508]

INFLUENCE OF NITROGEN TETROXIDE ON CELLULOSE STRUCTURE AND PROPERTIES,
PART 2: FORMATION OF CRYSTALLINE COMPLEXES UPON EXPOSURE OF CELLULOSE TO
SOLUTIONS OF NITROGEN TETROXIDE IN ACETIC ACID

Riga KHIMIYA DREVESINY in Russian No 3, May-Jun 83
(manuscript received 13 Aug 82) pp 19-22

GERT, Ye. V., SOKARRAS MORALES, A., MAKARENKO, M. V. and KAPUTSKIY, F. N.,
Scientific Research Institute of Physical Chemical Problems, Belorussian State
University imeni V. I. Lenin

[Abstract] An x-ray study was undertaken of unstable complexes of nitric and acetic acid with the composition $\text{HNO}_3 \cdot \text{CH}_3\text{COOH}$ and its effect on the process of swelling of cellulose in the mixture of nitrogen tetroxide and glacial acetic acid. Treatment of long fiber cotton with a mixture containing 5% N_2O_4 by volume causes no changes to the initial x-ray diagram. A basically new crystalline structure develops as a result of contact of cotton under these same conditions with a mixture containing 20% or 50% N_2O_4 . This structure differs significantly from the structure of the "swelling compounds" of cellulose produced directly in nitrogen tetroxide. There is a significant displacement of all interferences in the x-ray diagrams of the cellulose I into the area of smaller diffraction angles. The results indicate that when cellulose interacts with the system $\text{CH}_3\text{COOH}-\text{N}_2\text{O}_4$, both nitrogen tetroxide molecules and CH_3COOH molecules are inserted into the crystalline lattice of the polymer. The effect of N_2O_4 dissolved in CH_3COOH on cellulose leads to the formation of clearly expressed radiologically-complex structure differing basically from the structure of the initial material as well as the material swollen directly in N_2O_4 or HNO_3 . Figures 3; references 9: 6 Russian, 3 Western.
[300-6508]

UDC: 634.0.861.17

BLEACHING AND REFINEMENT OF CORD CELLULOSE FROM LARCH WOOD FIBER

Riga KHIMIYA DREVESINY in Russian No 3, May-Jun 83
(manuscript received 17 Jun 82) pp 23-26

ZARUDSKAYA, O. L., DOBRYNIN, N. A., BIRBROVER, N. M., KANAYLOVA, R. P.,
GRISHINA, T. A. and KUZINA, N. A., All-Union Scientific and Production
Association of the Paper Industry

[Abstract] The authors' association has developed and theoretically confirmed a process for cold refinement of prehydrolysis sulfate cellulose from pine fiber. A study was made of the basic indices of quality of larch cellulose during bleaching and cold refining by solutions of caustic soda and white alkali with 25% sulfide content under various conditions. Studies were performed on two specimens of sulfate prehydrolysis cellulose made of larch wood

fiber after bleaching. The results produced showed that, under identical refinement conditions with both white alkali and NaOH solution, as the concentration of hemicellulose increases in the alkaline solution to 4-8 g/l the content of α -cellulose in the cellulose after processing decreases by 0.4-1.0%. The nature of the change of α -cellulose content agrees well with the change in α -cellulose content and solubility of bleached cellulose in 10% NaOH solutions. Cold refinement, increasing the chemical purity of cellulose, significantly changes the physical and chemical properties of the substance, including swelling and density, which largely determine the technological suitability of cellulose for processing as cord fiber. The process of dissolution of hemicellulose during cold refinement of cellulose occurs in 5 to 10 minutes, its speed independent of the type of initial wood fiber. Specimens of cord cellulose from pine and larch bleached to equal viscosity have identically high molecular homogeneity. Figures 5; references 5 (Russian).
[300-6508]

UDC: 634.0.861.16:547.673.1

MECHANISM OF ACTION OF ANTHRAQUINONE IN ALKALINE COOKING

Riga KHIMIYA DREVESINY in Russian No 3, May-Jun 83
(manuscript received 7 Jul 82) pp 43-46

BUCNIN, M. Yu., MALKOV, Yu. A. and NEPENIN, Yu. N., All-Union Scientific and Production Union of the Paper Industry; Leningrad Wood Technology Academy imeni S. M. Kirov

[Abstract] A review is presented of the literature on the mechanism of action of anthraquinone as a catalyst of alkaline cooking including its mechanism of action in the process of delignification, particularly in sulfate cooking of cellulose. The authors feel that this process forms a sulfide-polysulfide oxidation-reduction system, the process being irreversible in an alkaline medium. The polysulfide which is formed can participate in reactions of oxidation of terminal carbonyl groups of hydrocarbons. On this basis, an oxidation-reduction scheme is suggested for the initial stage of sulfate cooking of cellulose. An experiment was performed to confirm the possibility of interaction of sodium sulfide and anthraquinone in sulfate cooking. The results of these experiments showed that sodium sulfide does indeed reduce anthraquinone during alkaline cooking. Anthraquinone can thus be considered responsible for accelerating delignification in sulfite cooking, while stabilization of carbohydrates against alkaline destruction is achieved by the formation of polysulfides. Figures 3; references 11: 5 Russian, 6 Western.
[300-6508]

ENZYMATIC HYDROLYSIS OF WOOD AND HAY POLYSACCHARIDES, PART 12: CHANGE IN SECONDARY LAYER STRUCTURE OF CELLULOSE FIBERS OBTAINED FROM BIRCH IN ENZYMATIC HYDROLYSIS

Riga KHIMIYA DREVESINY in Russian No 3, May-Jun 83
(manuscript received 14 Dec 82) pp 83-88

KATKEVICH, Yu. Yu., VEVERE, P. Ya. and PENDERE, M. K., Institute of Wood Chemistry, Latvian SSR Academy of Sciences

[Abstract] A study is presented of the changes occurring in the submicroscopic structure of secondary envelopes in the process of enzymatic hydrolysis. Cellulose was obtained from birch fiber with a yield of 36% by soda cooking. The cellulose fibers were then hydromechanically worked for 85 hours to achieve 73% delamination of the cellulose fibers. Enzymatic preparations were prepared to study the mechanism of splitting of fibers and the enzymatic hydrolysis of cellulose fibers was performed in vessels equipped with a semi-permeable membrane. The studies showed that in the secondary envelopes of the cellulose fibers within the first hour of enzymatic hydrolysis transverse cracks begin to form. After two hours exposure to cellulose the cracks are more numerous and deeper. At 6 hours the cellulose fibers break down into individual sections. The process of enzymatic hydrolysis occurs more rapidly in the death of the envelope than in the longitudinal direction of the fiber. Electron photomicrographs illustrate the changes which occur. IR spectroscopic and x-ray diffractometric data demonstrate that the degree of ordering of cellulose in the unhydrolyzed residues decreases very little and, only in the last stages when about 5% cellulose remains, does it decrease from 0.65 to 0.59, the size of crystals decreasing from 3.8 to 3.6 nm. Figures 7; references 9: 6 Russian, 3 Western.
[300-6508]

UDC: 634.0.842:54-126

STUDY OF POLYMERIZATION KINETICS OF MONOMERS IN WOOD FIBER MASS, PART 1: POLYMERIZATION OF 1,3-DIPHENYL-1-BUTENE IN POPLAR TIMBER

Riga KHIMIYA DREVESINY in Russian No 3, May-Jun 83
(manuscript received 16 Mar 82) pp 102-107

BLAZHKOVA, A., LAPCHIK, L., GRIVIKOVA, Y., GLAVATY, M. and ONDREYICHKA, M., Slovak Polytechnical Institute (Bratislava, CSSR)

[Abstract] A study is made of the possibility of modifying poplar wood fiber with a styrene-1,3-diphenyl-1-butene dimer. The free radicals necessary for initiation of polymerization are formed in the process of swelling of the wood fiber in the monomer. Upon swelling of macromolecular substances under certain conditions breaking of polymer chains may occur under the influence of internal pressure. The influence of wood fiber moisture content, type of mixed solvent and presence of oxygen on degree of monomer conversion in the wood

fiber is studied. A wood-plastic material was produced from bars of poplar wood fiber measuring 1.5 x 1.0 x 0.2 cm dried in a vacuum drier at 45°C at low pressure to constant mass. The polymerizable agent used was a styrene dimer with b.p.=181.2°C, $n_D^{25} = 1.5930$. The solvent in polymerization was n-octyl alcohol, n-propyl alcohol plus pyridine. Photomicrographs are presented of the wood structure. The degree of conversion of the dimer was found to increase with increasing water content in the wood pulp. The quantity of copolymer formed increased in the presence of the solvent. The maximum conversion of styrene dimer was achieved by the use of poplar wood fiber with initial moisture content 19% in the presence of n-propyl alcohol with a monomer-to-solvent ratio of 9 to 1. Figures 7; references 20: 4 Russian, 16 Western.
[300-6508]

UDC: 532.783+547.539.1+547.622

LIQUID CRYSTALS CONTAINING FLUORINE, PART 8: 4-PERFLUOROALKYL-4'-ALKYL-AMINODIPHENYLS

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 19, No 5, May 83
(manuscript received 26 Jul 82) pp 1048-1053

FAILKOV, Yu. A., SHELYAZHENKO, S. V. and YAGUPOL'SKIY, L. M., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Continuing studies to determine the influence of fluorine-containing substituents on mesomorphic properties of compounds, the authors synthesized fluorinated analogs of two alkyl derivatives of cyanodiphenyl having the properties of nematic liquid crystals - 4-propyl-4'-cyanodiphenyl and 4-hexyl-4'-cyanodiphenyl. The perfluoroalkylcyanodiphenyls produced do not have mesomorphic properties. The authors encountered this phenomenon of disappearance of mesomorphism as a result of substitution of terminal alkyl groups in the molecule of liquid crystals with perfluoroalkyl groups of opposite electron structure in studying the properties of fluorinated analogs of 4-methoxybenzylidene-4'-butylaniline and p-alkoxybenzoic acids. It was found that 4-trifluoromethoxybenzylidene-4'-perfluorobutylaniline, as well as 4-polyfluoroalkoxybenzoic acids do not have the properties of liquid crystals. When molecules of liquid crystals containing conjugate aromatic systems are constructed, one must therefore consider the electron effects of the terminal substituents and their interaction. Replacement of a hydrogen atom with fluorine in alkyl radicals leads to a change in their electron nature and a significant increase in polarity. Therefore when there is a perfluoroalkyl radical in a conjugate aromatic system, an electron donor terminal group must be added to yield mesomorphic properties. References 19: 8 Russian, 11 Western.
[299-6508]

STUDY OF THERMOMECHANICAL PROPERTIES OF CRYSTALLIZATION PRODUCTS OF LIGHT-SENSITIVE GLASS AS A FUNCTION OF HEAT TREATMENT CONDITIONS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 270, No 1, May 83
(manuscript received 1 Sep 82) pp 154-157

BEREZHNOY, A. I., KRASNIKOVA, M. D., YERMAKOV, N. I. and REMIZOVA, A. A.,
Ryazan' State Pedagogics Institute

[Abstract] A study is presented of the mechanical and thermal properties of lithium aluminosilicate photosittals as a function of the composition and heat treatment conditions in order to seek out optimal photosittal synthesis conditions yielding products with predefined coefficient of linear expansion. The photosittal specimens studied had chemical composition similar to that presented in British patent 875367, 1960. The specimens were prepared as flat plates which were irradiated and crystallized by various methods at 570 to 850°C, one hour. X-ray studies of the specimens were performed with a $\text{CuK}\alpha$ radiation scintillation counter and nickel filter. Mechanical properties were determined by bending. Young's modulus was calculated. X-ray phase analysis identified two crystalline phases: lithium metasilicate and β -spodumene. The content of crystalline phase was as high as 70% for specimens crystallized at the higher temperatures. The content of lithium metasilicate increased to 35%, then decreased to 26% as temperature rose. The coefficient of thermal expansion was low. Young's modulus was found to depend on the type of crystalline phases, always being higher than the initial glass. The data indicated that as crystallization temperature increases, there is an increase in the content of crystalline phase, reaching 70% for specimens crystallized at 780°C. The maximum value of Young's modulus, 8500 kg/mm², is observed for specimens crystallized at about 710°C. The low value of thermal expansion results primarily from the fact that the main crystalline phase is β -spodumene. Figures 2; references 6: 3 Russian, 3 Western.

[283-6508]

CSO: 1841

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